

**Unified Enantioselective, Convergent Synthetic Approach Toward the
Furanobutenolide-Derived Polycyclic Norcembranoid Diterpenes: Synthesis of a
Series of Ineleganoloids by Oxidation State Manipulation of the Carbocyclic Core**

Robert A. Craig, II, Russell C. Smith, Jennifer L. Roizen,
Amanda C. Jones, Scott C. Virgil, and Brian M. Stoltz*

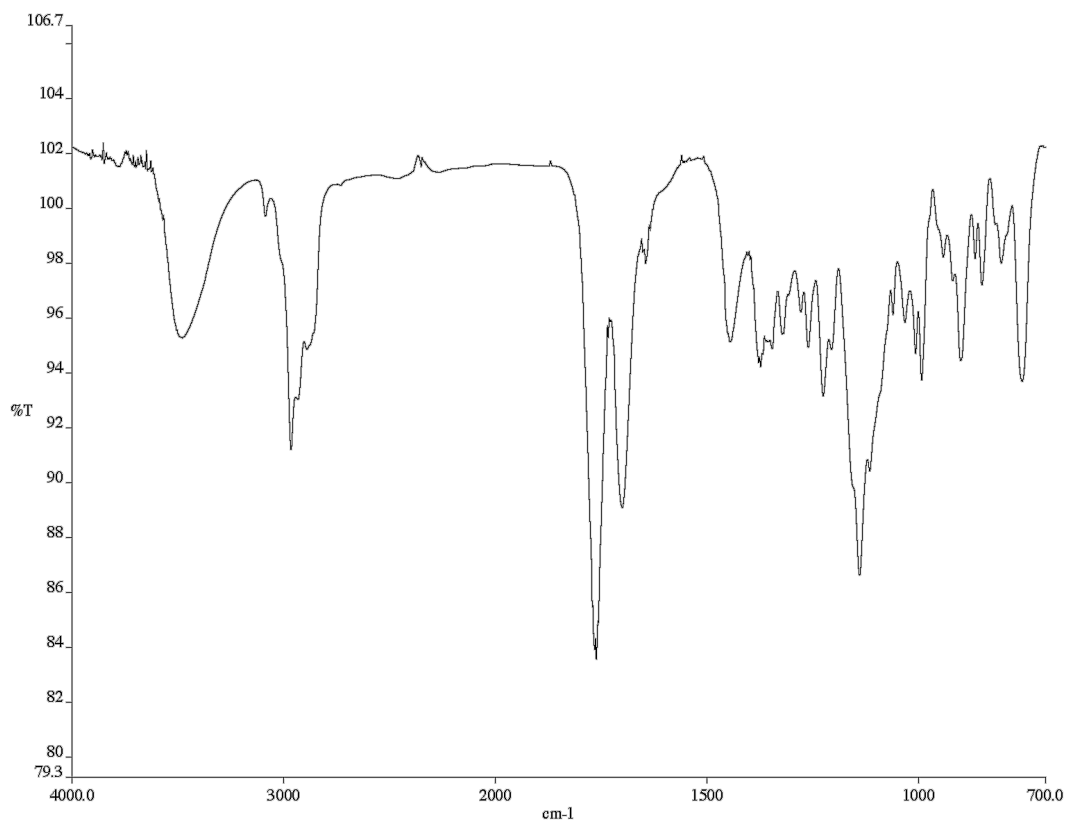
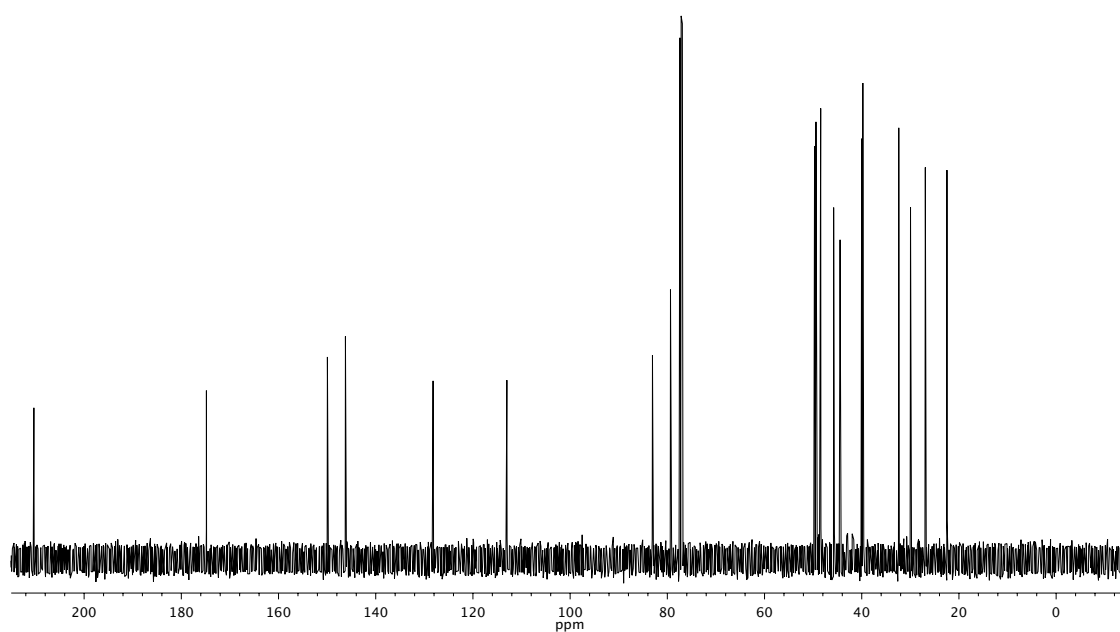
*Warren and Katharine Schlinger Laboratory for Chemistry and Chemical Engineering,
Division of Chemistry and Chemical Engineering, California Institute of Technology, MC
101-20, Pasadena, CA 91125, U.S.A.*

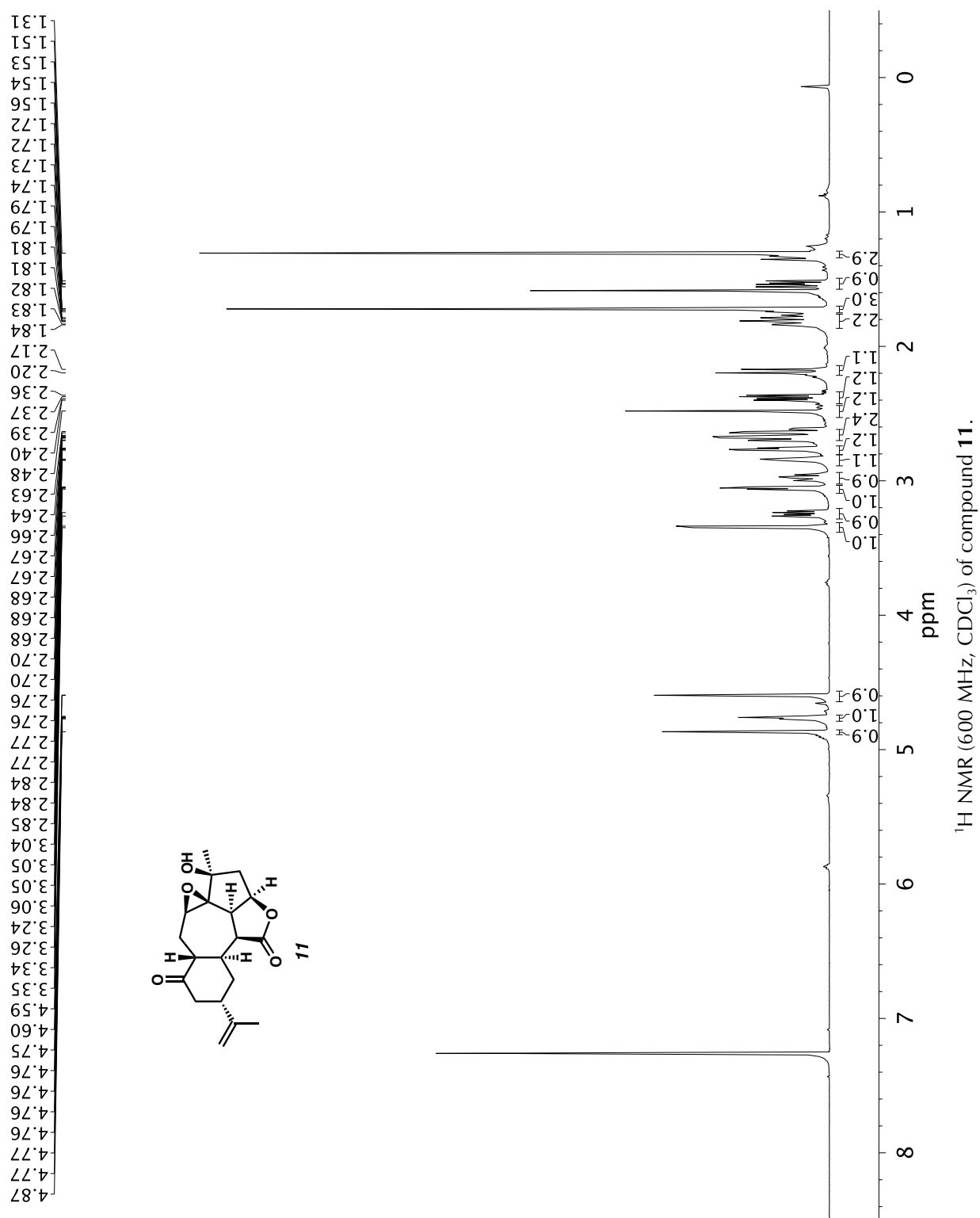
Table of Contents

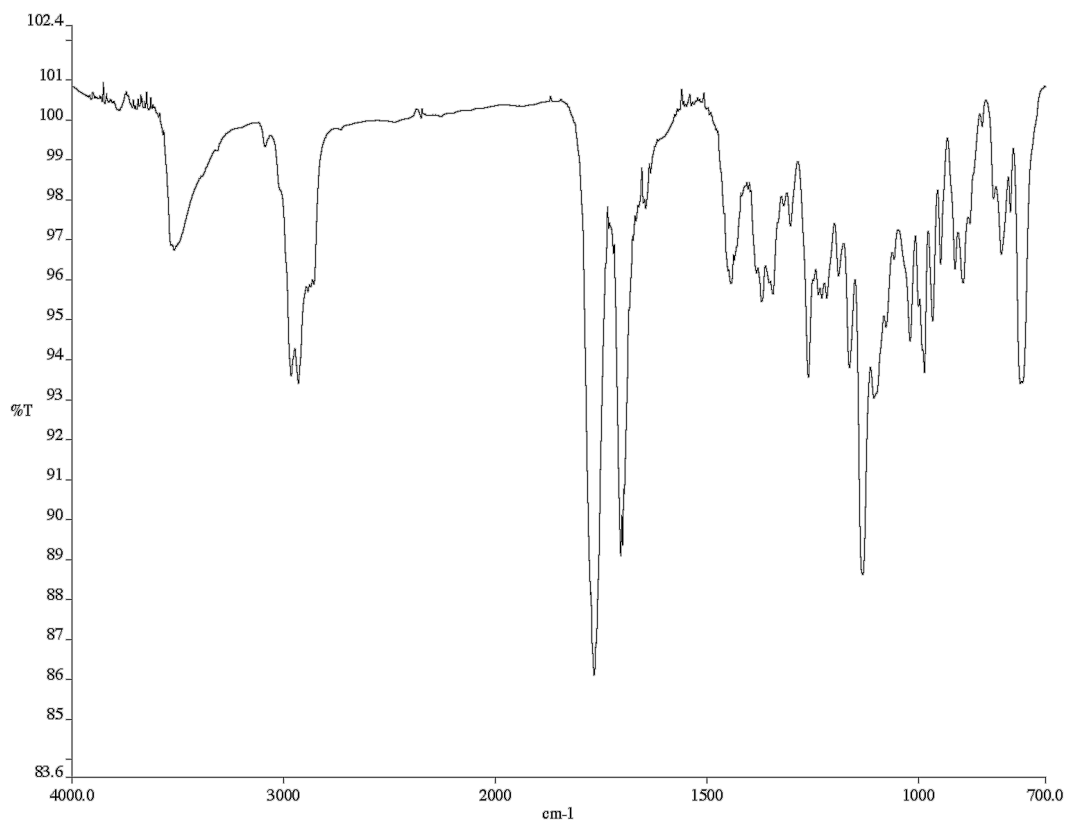
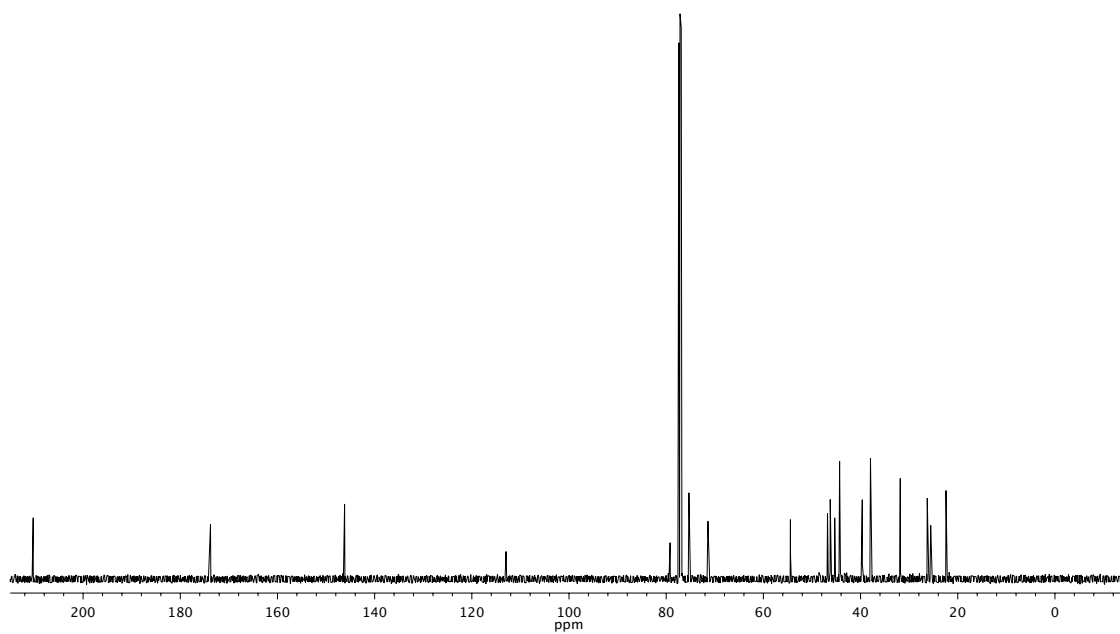
| | |
|---|-----|
| ¹ H, ¹³ C, and IR spectra for Allylic Alcohol 12 | S3 |
| ¹ H, ¹³ C, and IR spectra for Epoxide 11 | S5 |
| ¹ H, ¹³ C, and IR spectra for Bromide 15 | S7 |
| ¹ H, ¹³ C, and IR spectra for 2 <i>H</i> - <i>ent</i> -Ineleganolide (8) | S9 |
| ¹ H, ¹³ C, and IR spectra for Diketone 16 | S11 |
| ¹ H, ¹³ C, and IR spectra for Silyl Ether 17 | S13 |
| ¹ H, ¹³ C, and IR spectra for Epoxide 18 | S15 |
| ¹ H, ¹³ C, and IR spectra for Diol 19 | S17 |
| ¹ H, ¹³ C, and IR spectra for Allylic Alcohol 24 | S19 |
| ¹ H, ¹³ C, and IR spectra for Silyl Ether 25 | S21 |
| ¹ H, ¹³ C, and IR spectra for Bis-silyl Ether 26 | S23 |
| ¹ H, ¹³ C, and IR spectra for Allylic Silyl Ether 30 | S25 |
| ¹ H, ¹³ C, and IR spectra for Unsaturated Lactone 31 | S27 |
| ¹ H, ¹³ C, and IR spectra for Epoxide 32 | S29 |
| ¹ H, ¹³ C, and IR spectra for Diol 36 | S31 |

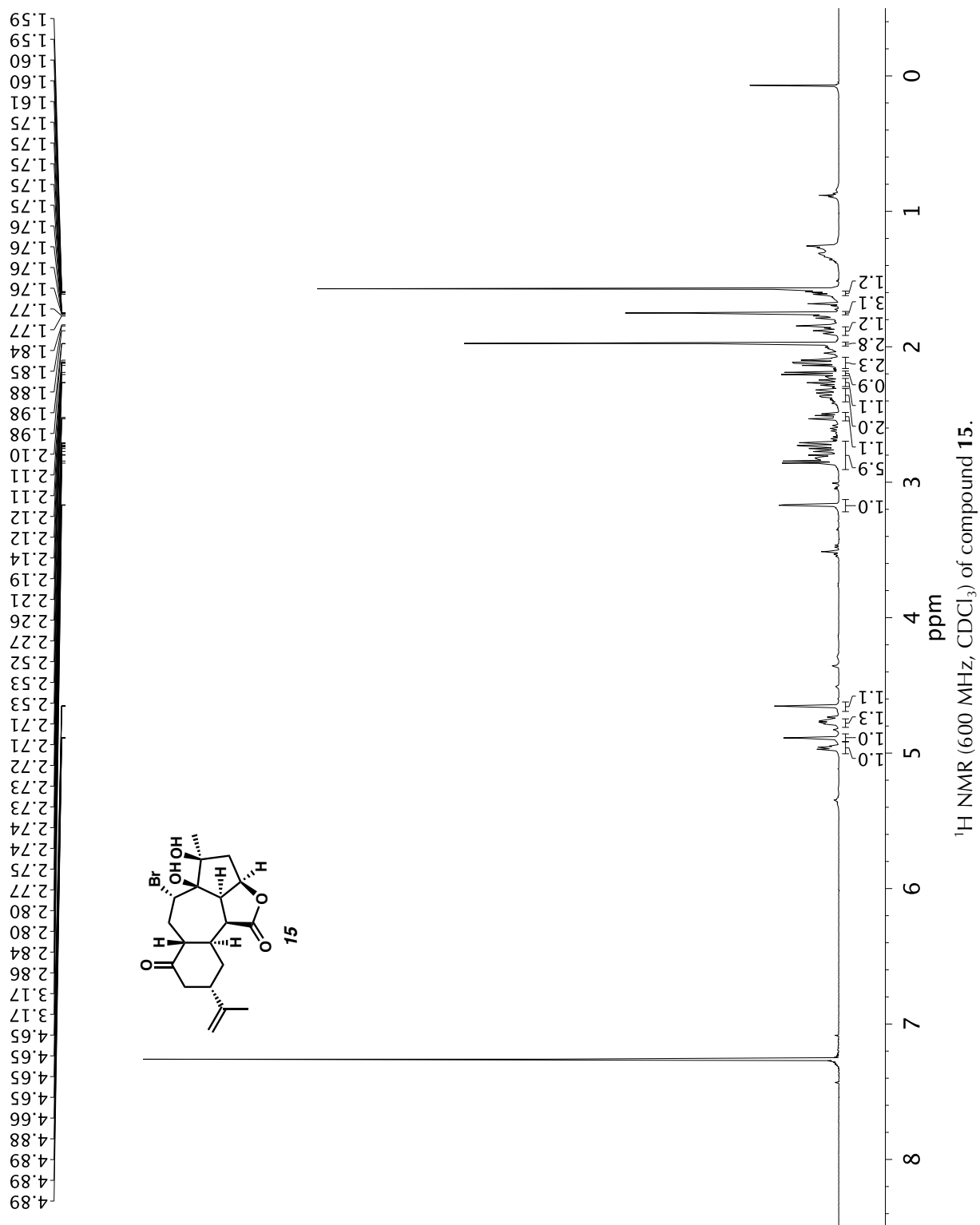
| | |
|---|-----|
| ^1H , ^{13}C , and IR spectra for Ketone 37 | S33 |
| ^1H , ^{13}C , and IR spectra for Diol 39 | S35 |
| ^1H , ^{13}C , and IR spectra for Ketone 40 | S37 |
| ^1H , ^{13}C , and IR spectra for Silyl Enol Ether 41 | S39 |
| ^1H , ^{13}C , and IR spectra for Bis-silyl Ether 43 | S41 |
| ^1H , ^{13}C , and IR spectra for Lactol 45 | S43 |
| ^1H , ^{13}C , and IR spectra for Lactol 46 | S45 |
| ^1H , ^{13}C , and IR spectra for Allylic Alcohol 47 | S47 |
| ^1H , ^{13}C , and IR spectra for Bis-silyl Ether 48 | S49 |
| ^1H , ^{13}C , and IR spectra for Epoxide 49 | S51 |
| ^1H , ^{13}C , and IR spectra for Acetal 50 | S53 |
| ^1H , ^{13}C , and IR spectra for Vinylogous Diketone 55 | S55 |
| ^1H , ^{13}C , and IR spectra for Polyunsaturated Diketone 56 | S57 |
| ^1H , ^{13}C , and IR spectra for Dienol Ether 57 | S59 |
| ^1H , ^{13}C , and IR spectra for Dienol Acetate 58 | S61 |
| ^1H , ^{13}C , and IR spectra for α -Bromolactone 63 | S63 |
| ^1H , ^{13}C , and IR spectra for <i>ent</i> -Dehydroisoinoleganolide (65) | S65 |
| ^1H , ^{13}C , and IR spectra for <i>ent</i> -Didehydroisoinoleganolide (66) | S67 |

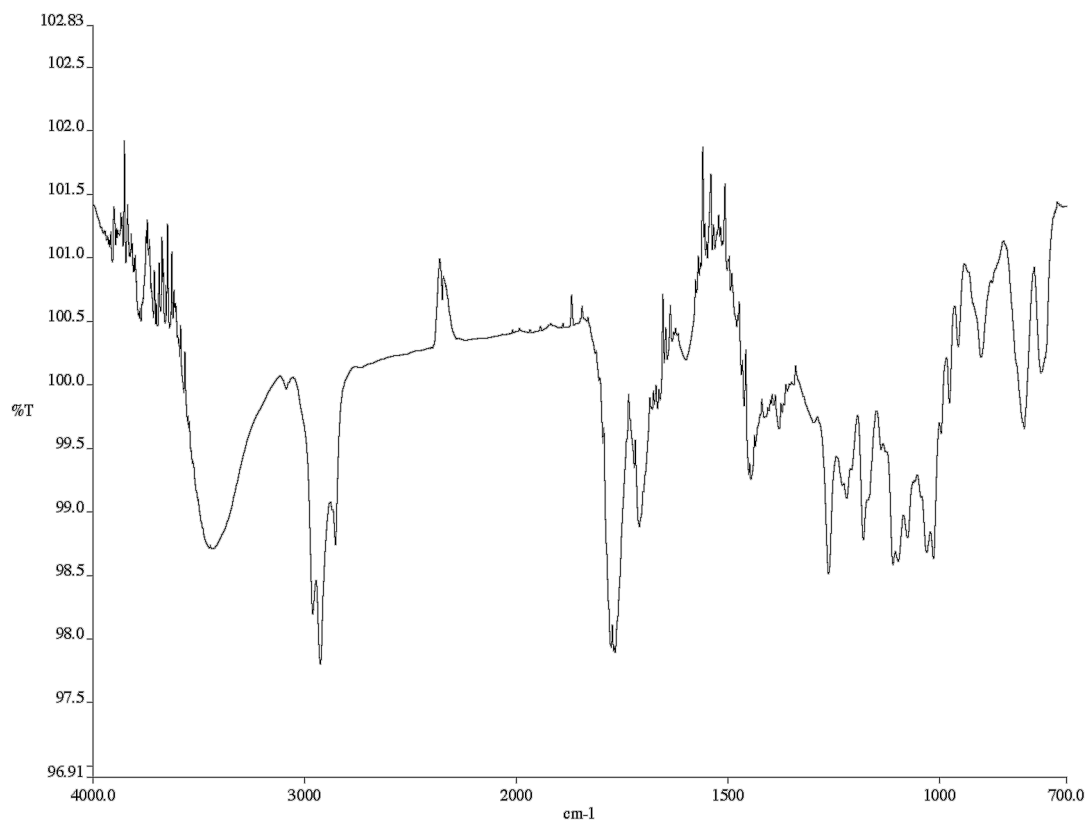
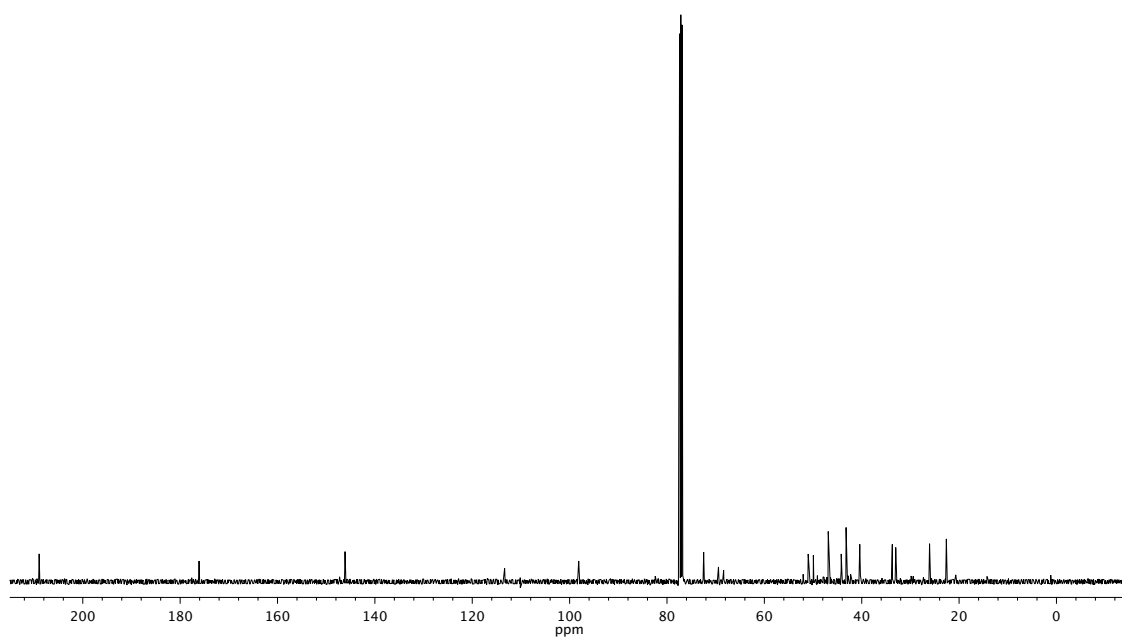


Infrared spectrum (Thin Film, NaCl) of compound **12**.¹³C NMR (126 MHz, CDCl₃) of compound **12**.

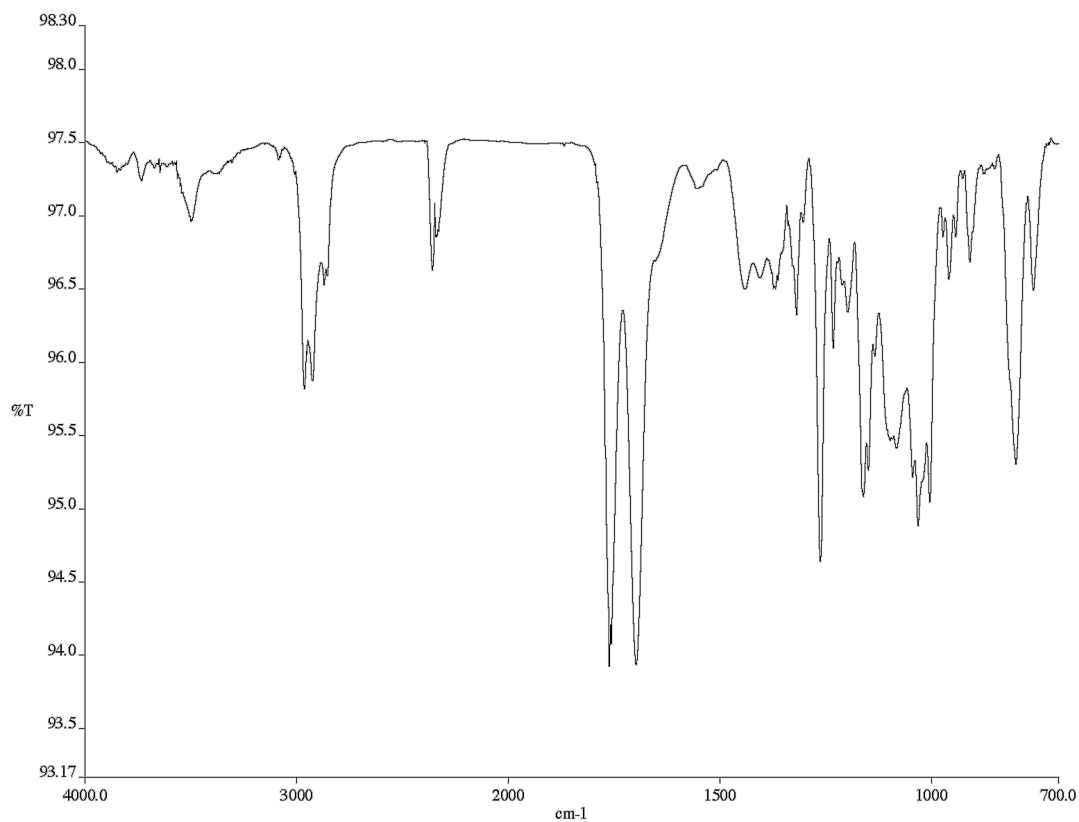
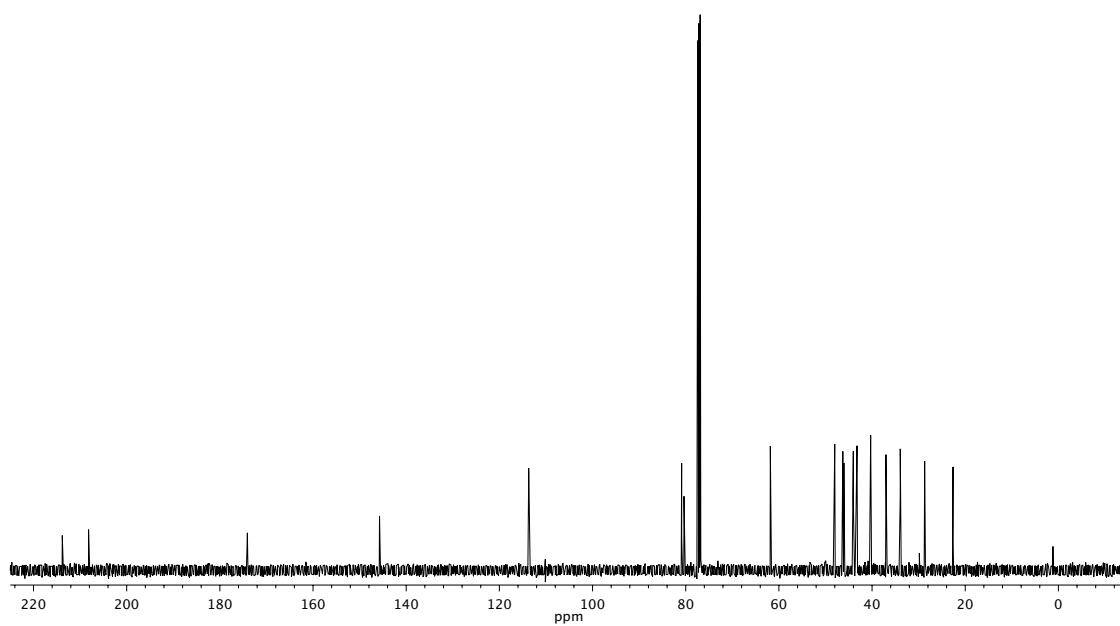


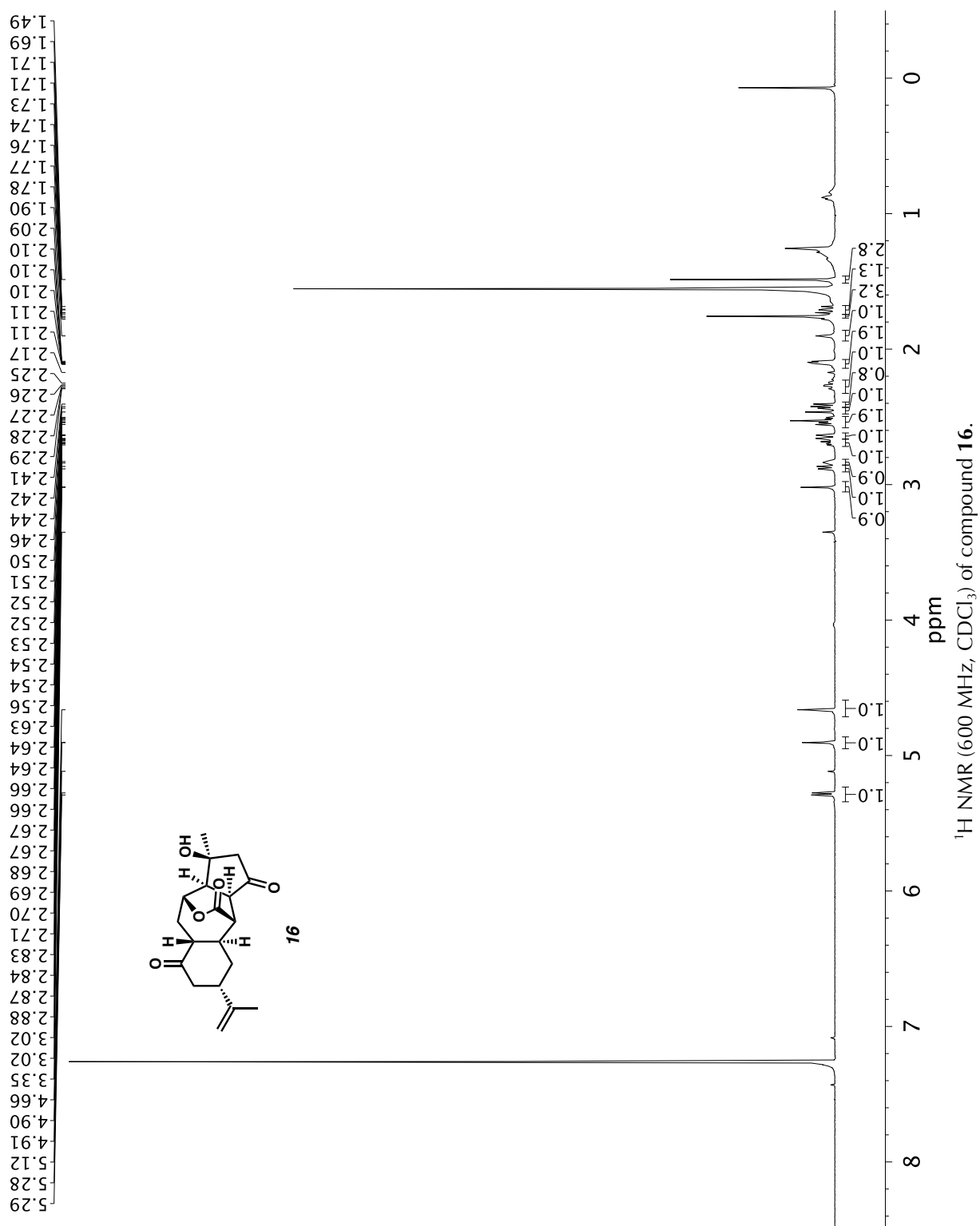
Infrared spectrum (Thin Film, NaCl) of compound **11**.¹³C NMR (126 MHz, CDCl₃) of compound **11**.

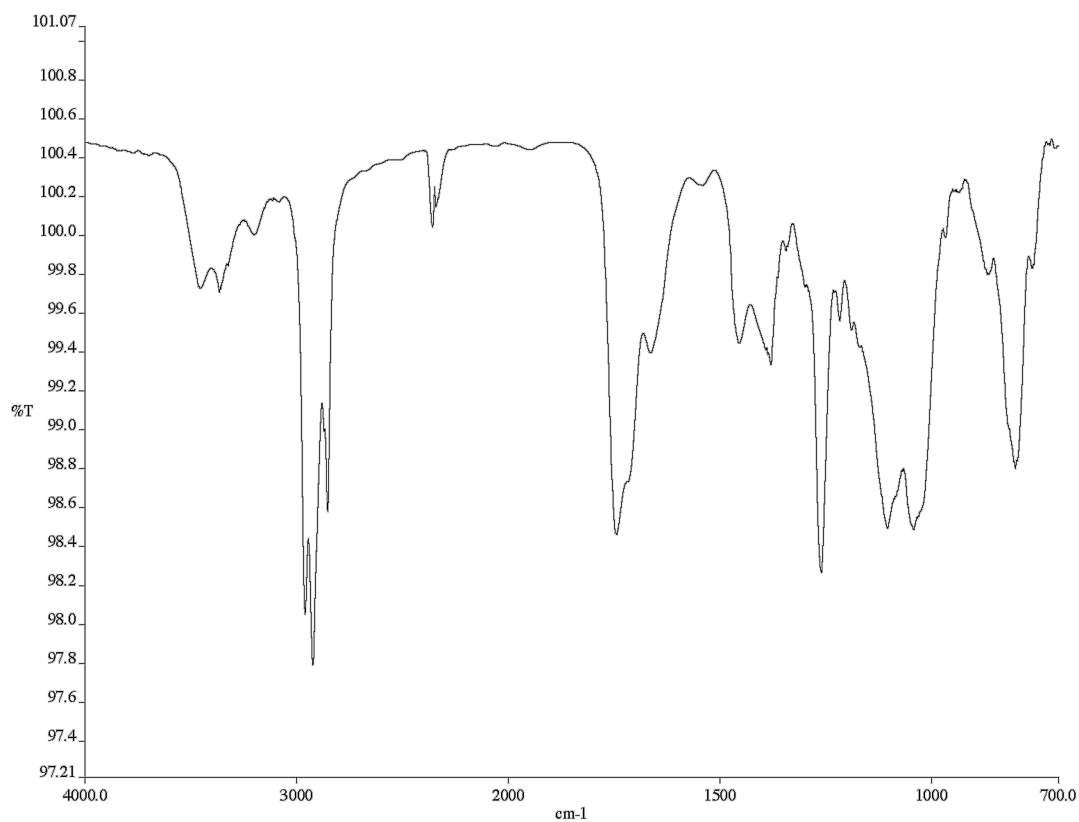
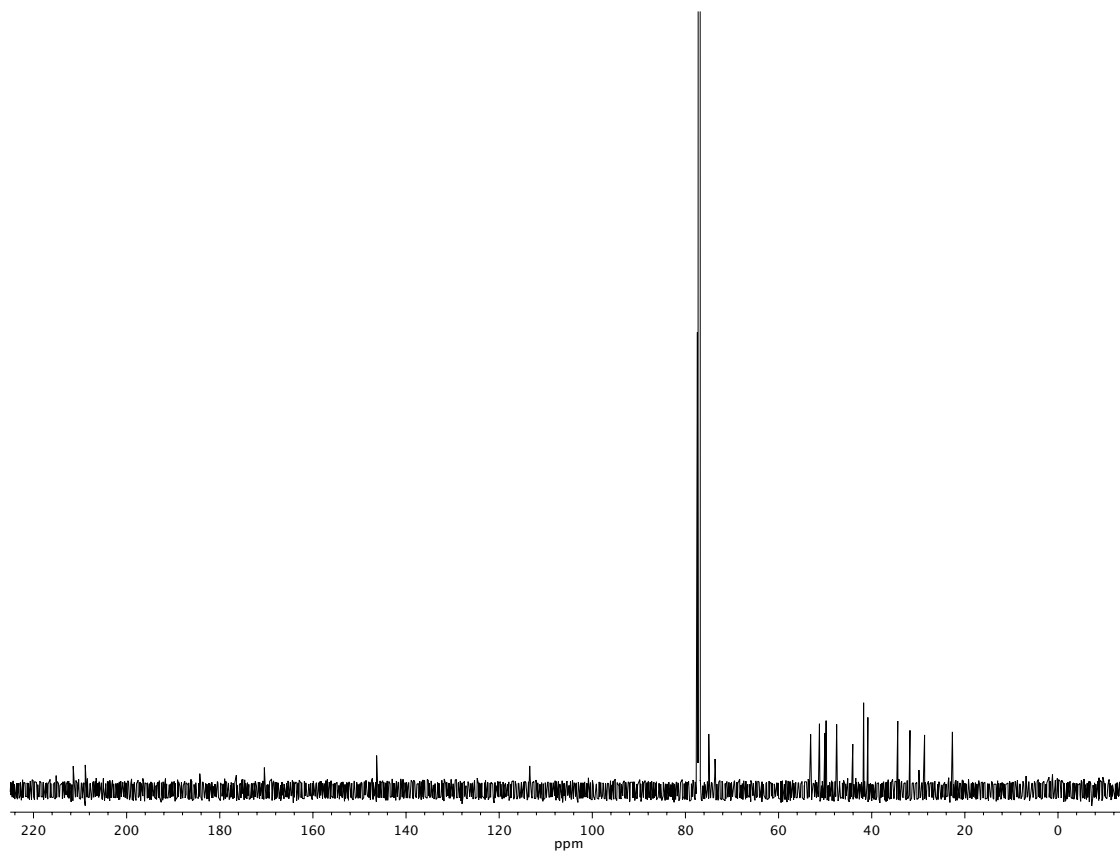


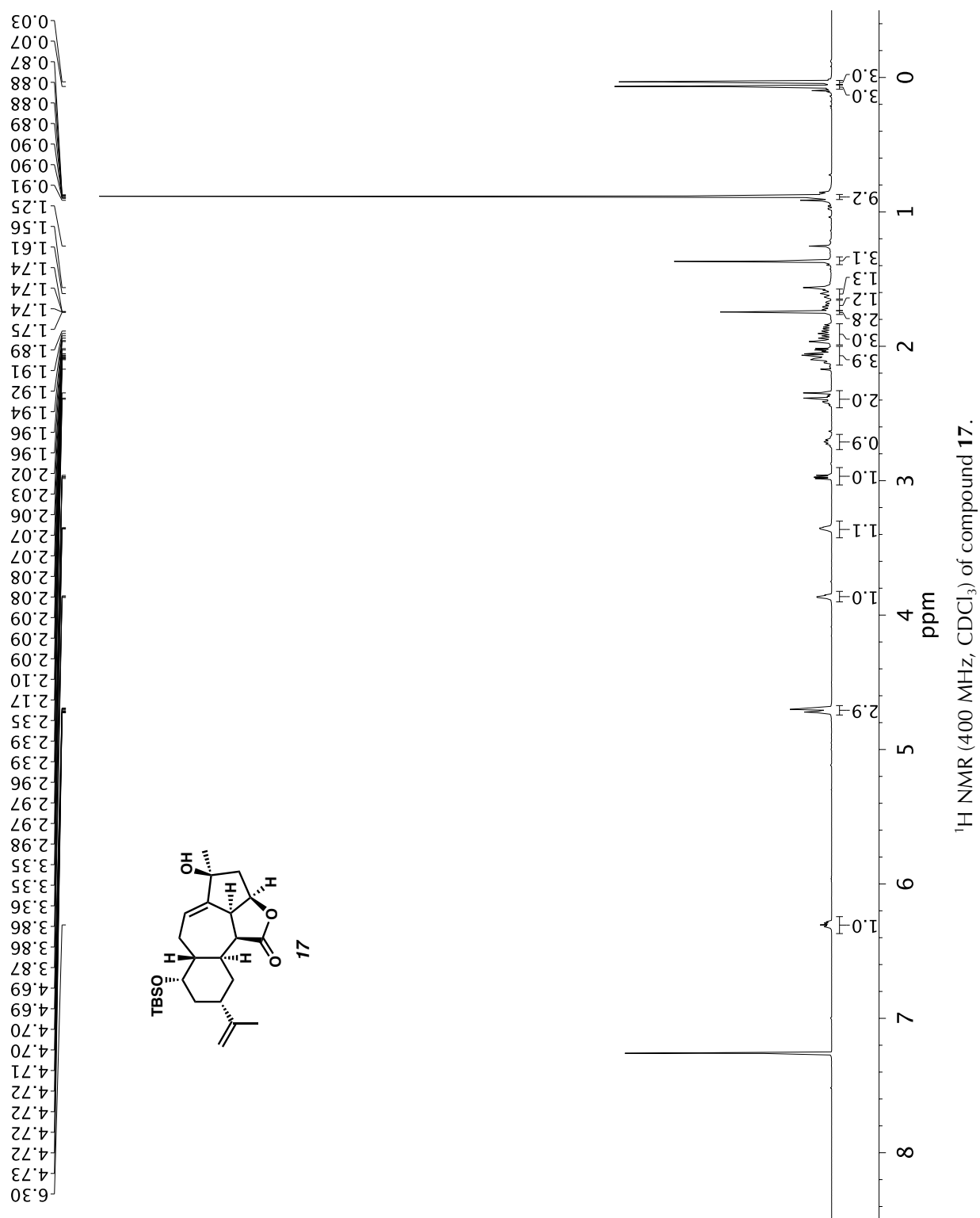
Infrared spectrum (Thin Film, NaCl) of compound **15**.¹³C NMR (126 MHz, CDCl₃) of compound **15**.

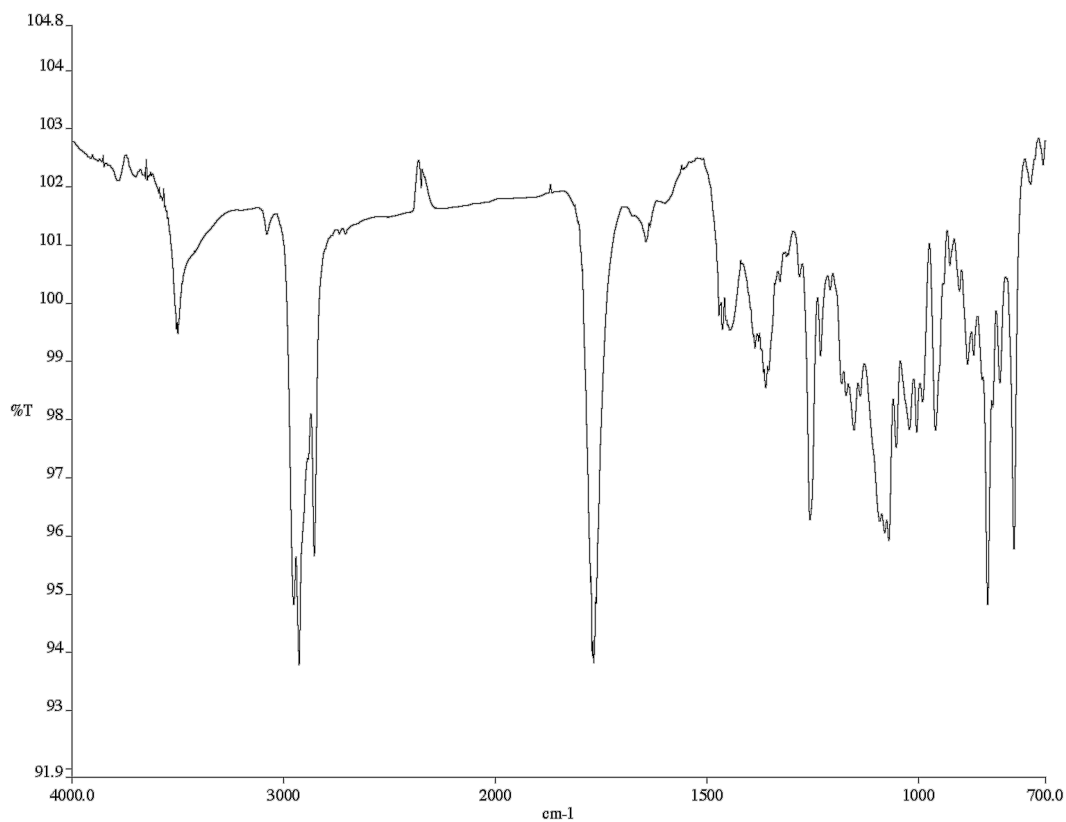
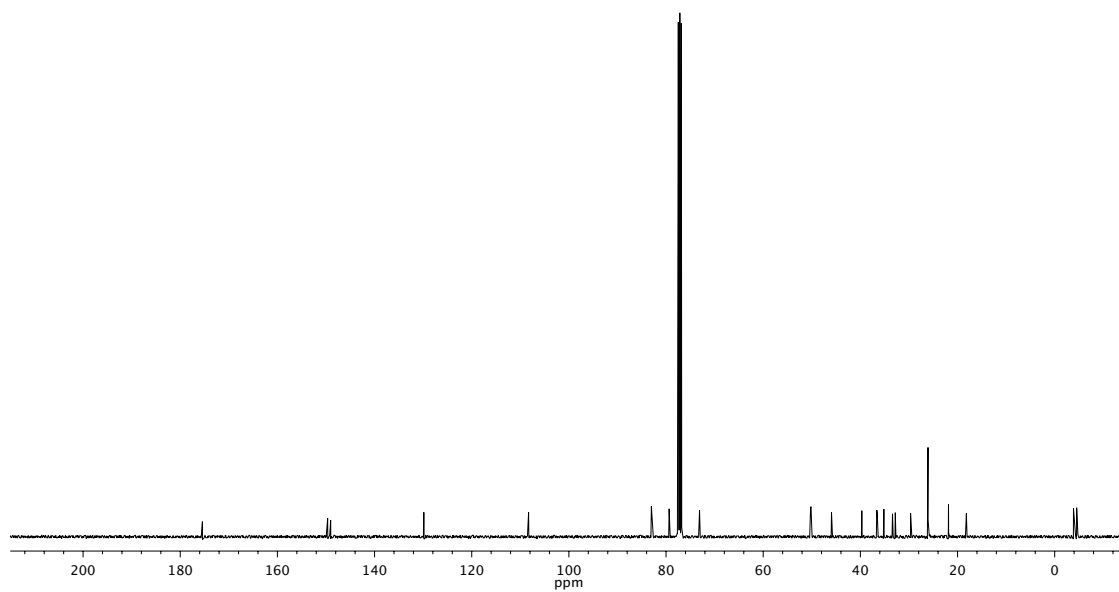


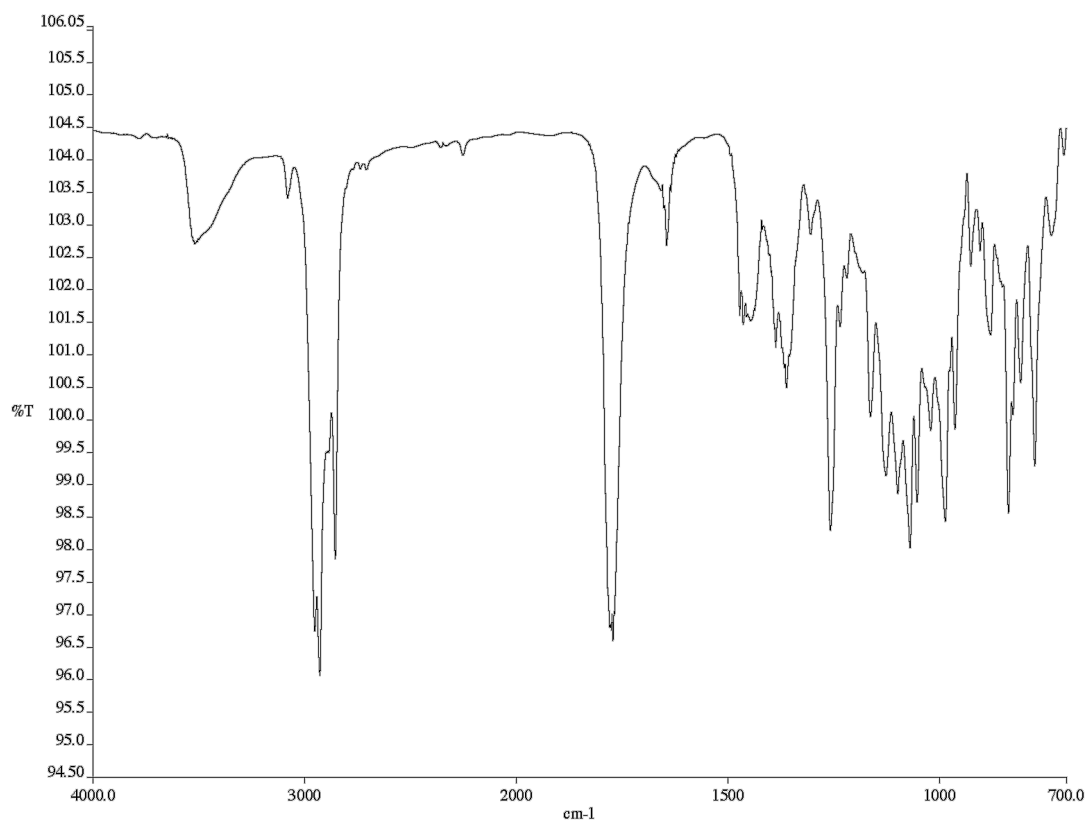
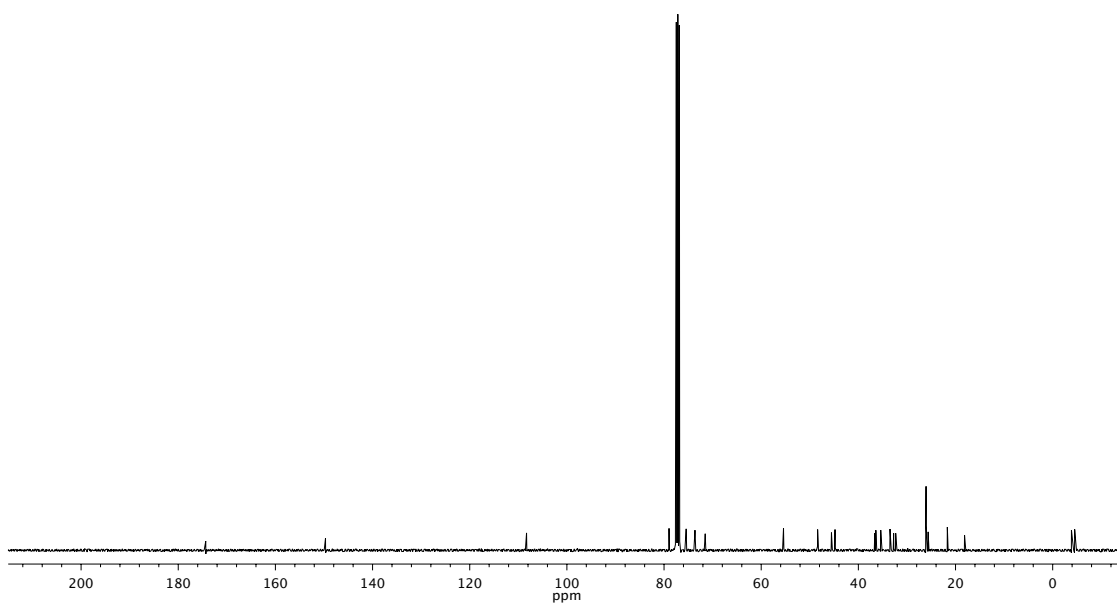
Infrared spectrum (Thin Film, NaCl) of compound **8**.¹³C NMR (126 MHz, CDCl₃) of compound **8**.

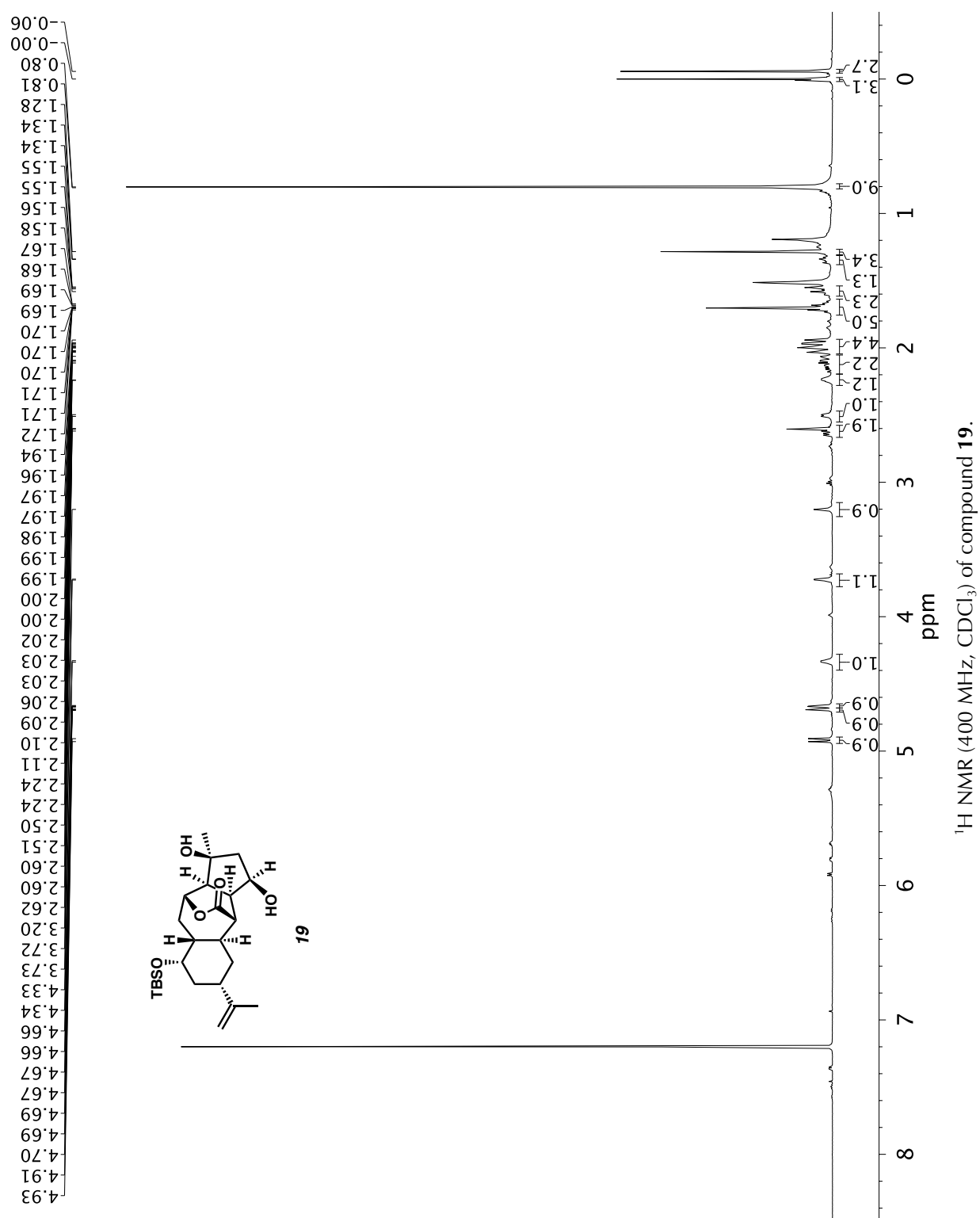


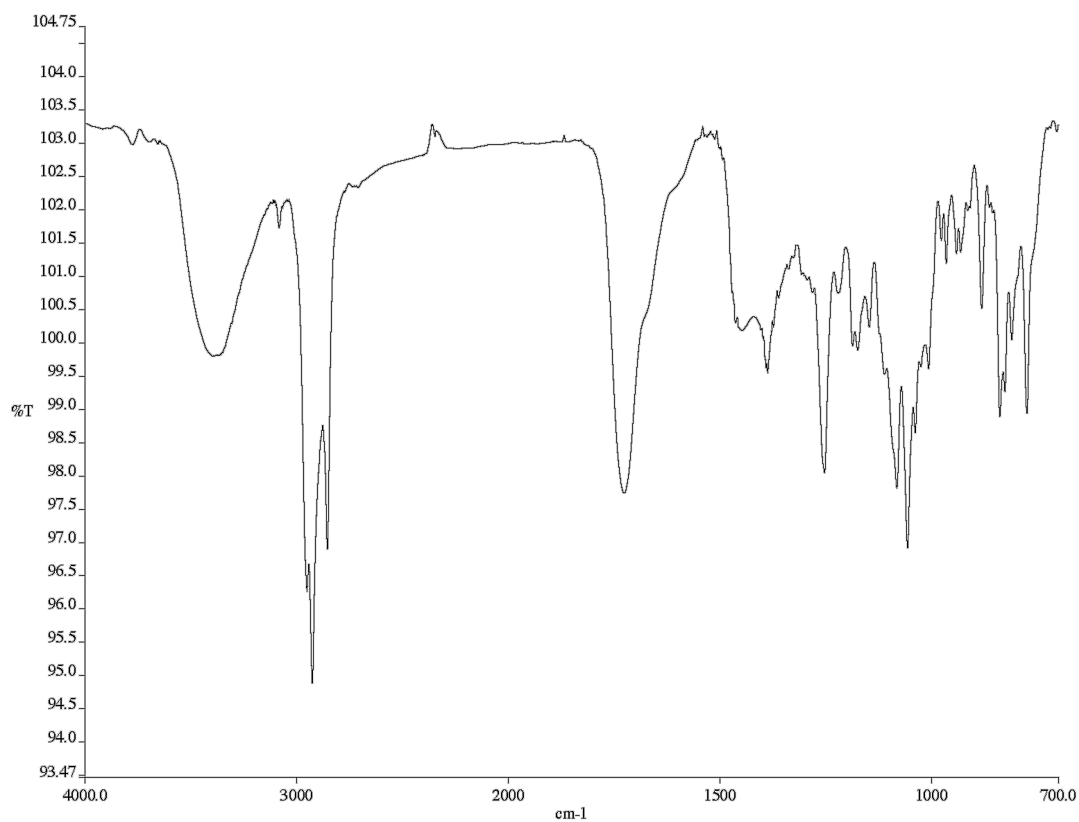
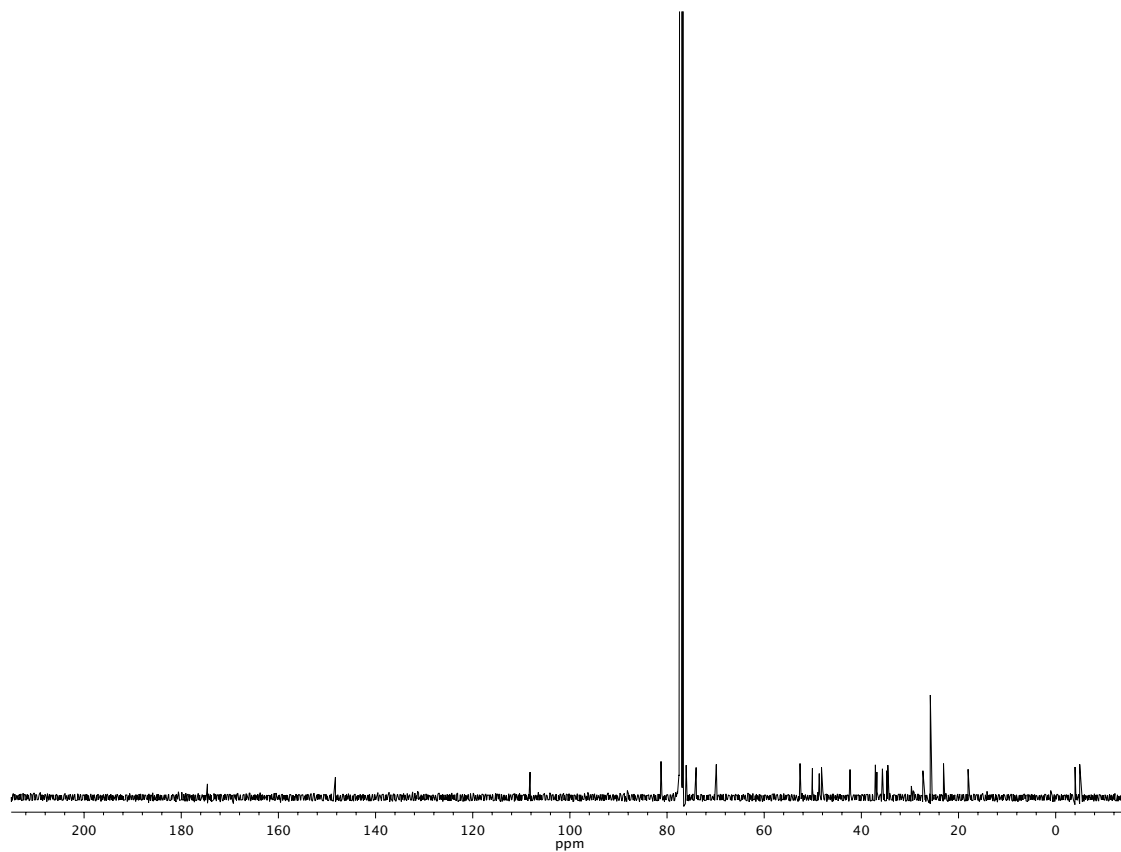
Infrared spectrum (Thin Film, NaCl) of compound **16**.¹³C NMR (126 MHz, CDCl₃) of compound **16**.



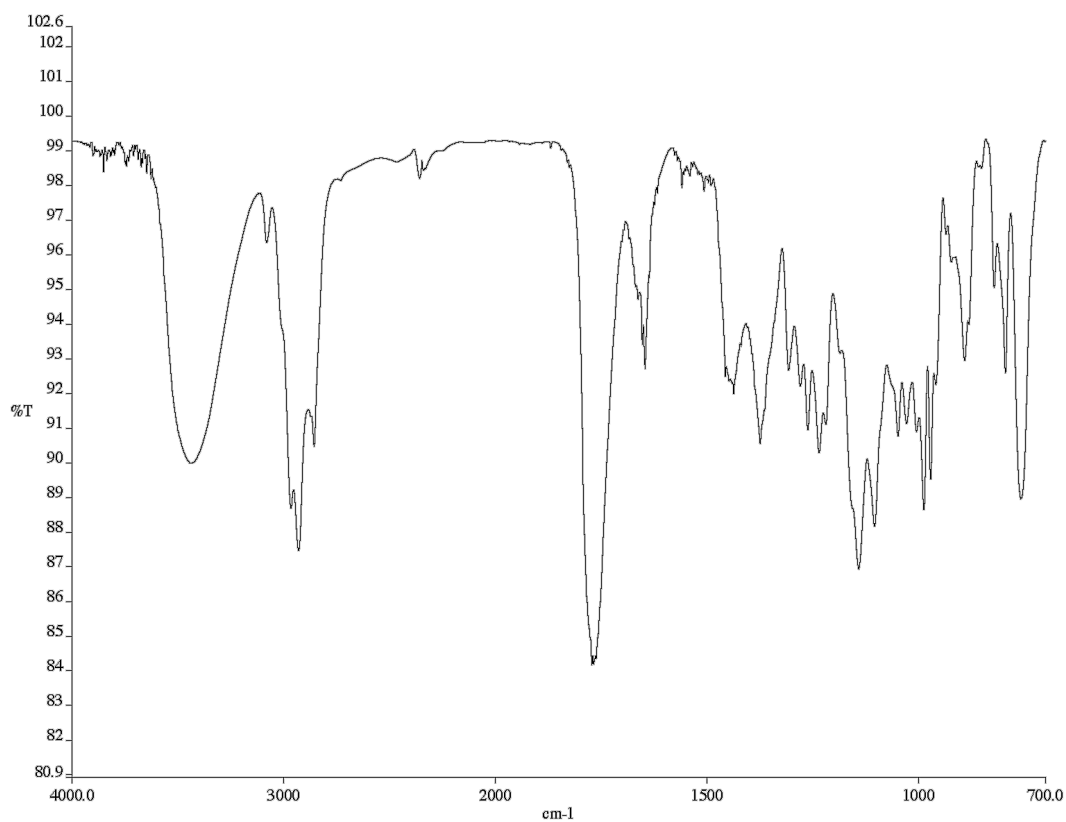
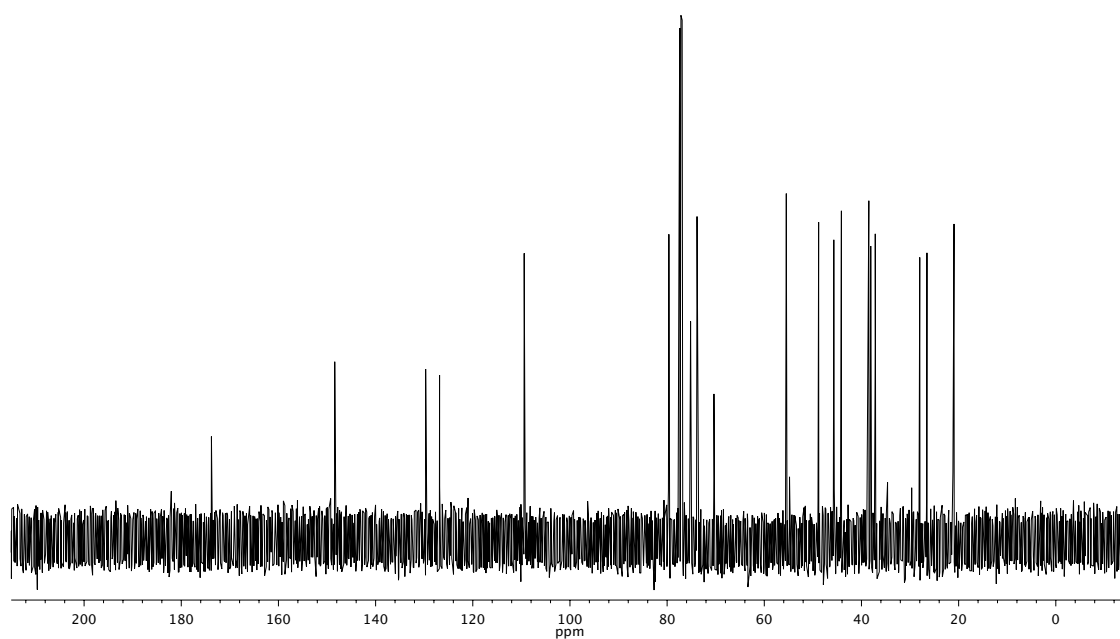
Infrared spectrum (Thin Film, NaCl) of compound **17**. ^{13}C NMR (101 MHz, CDCl_3) of compound **17**.

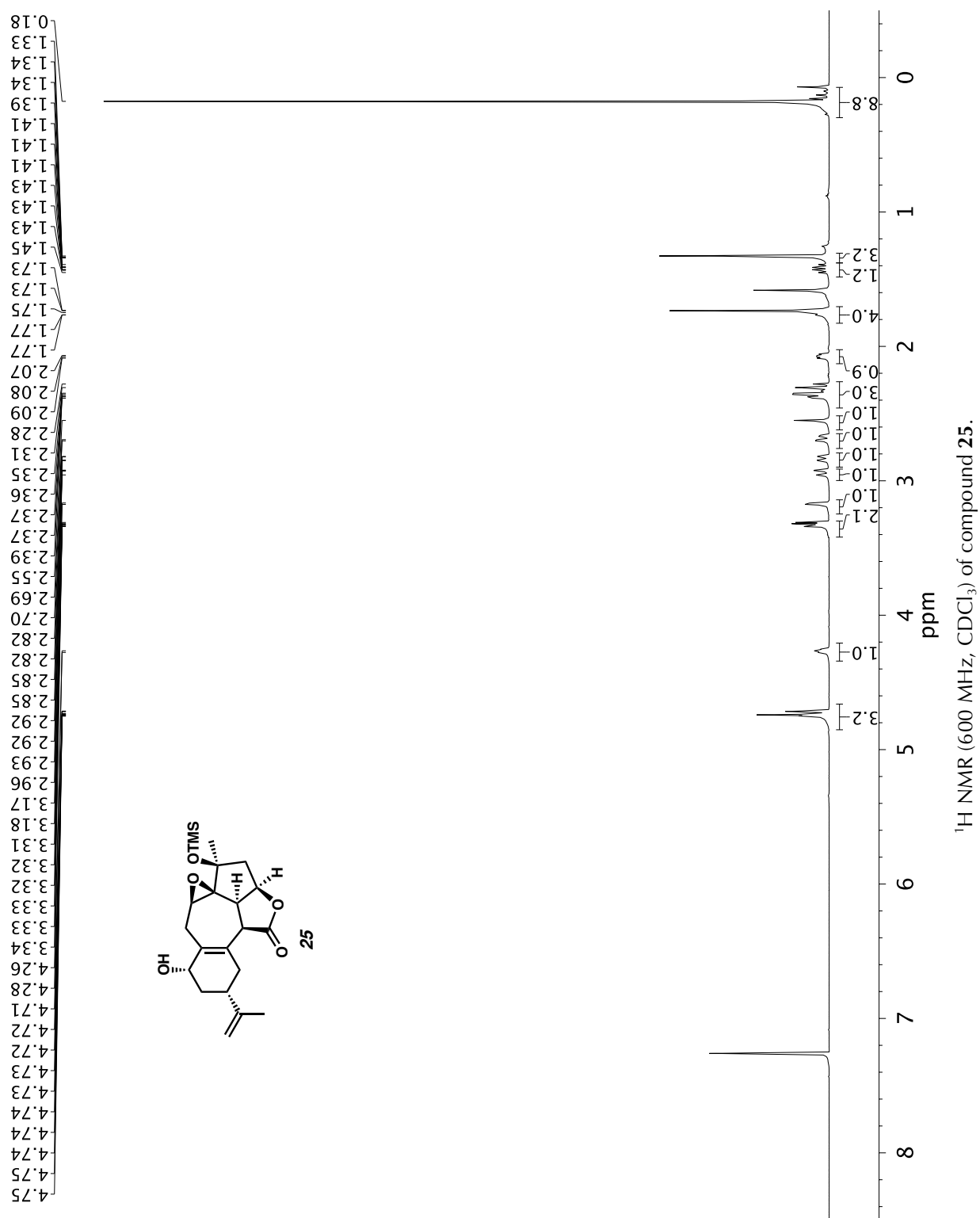
Infrared spectrum (Thin Film, NaCl) of compound **18**.¹³C NMR (101 MHz, CDCl₃) of compound **18**.

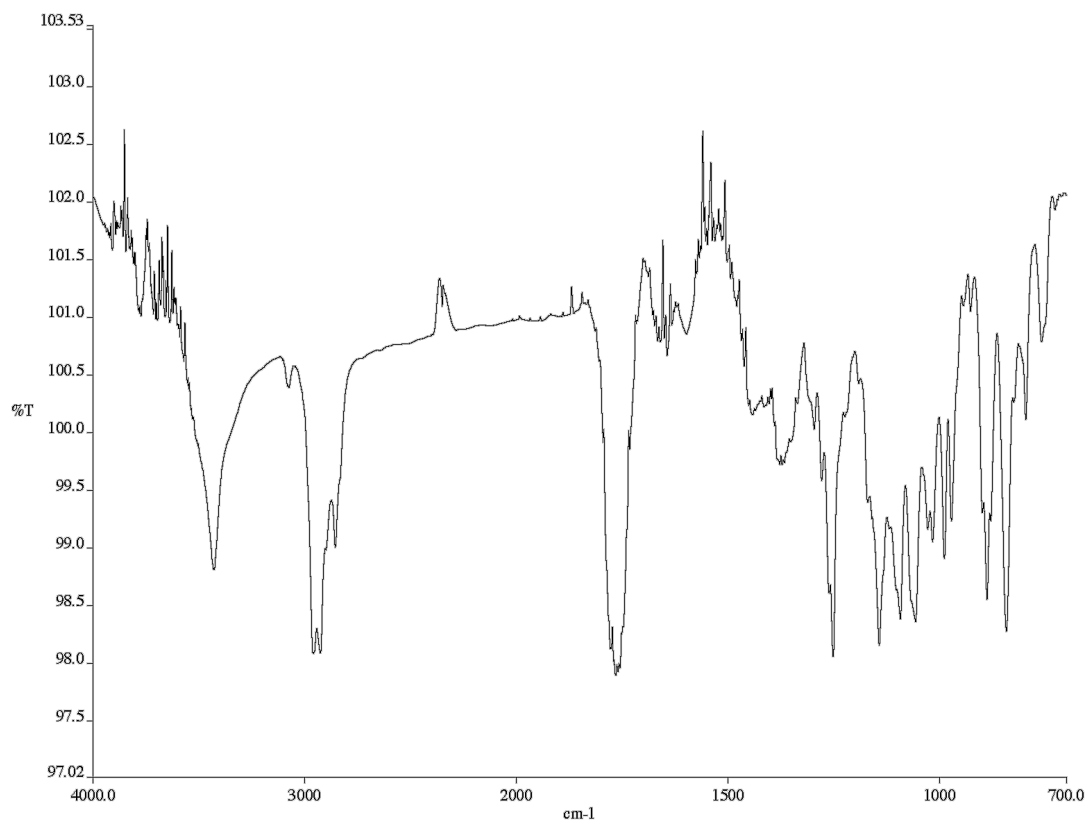
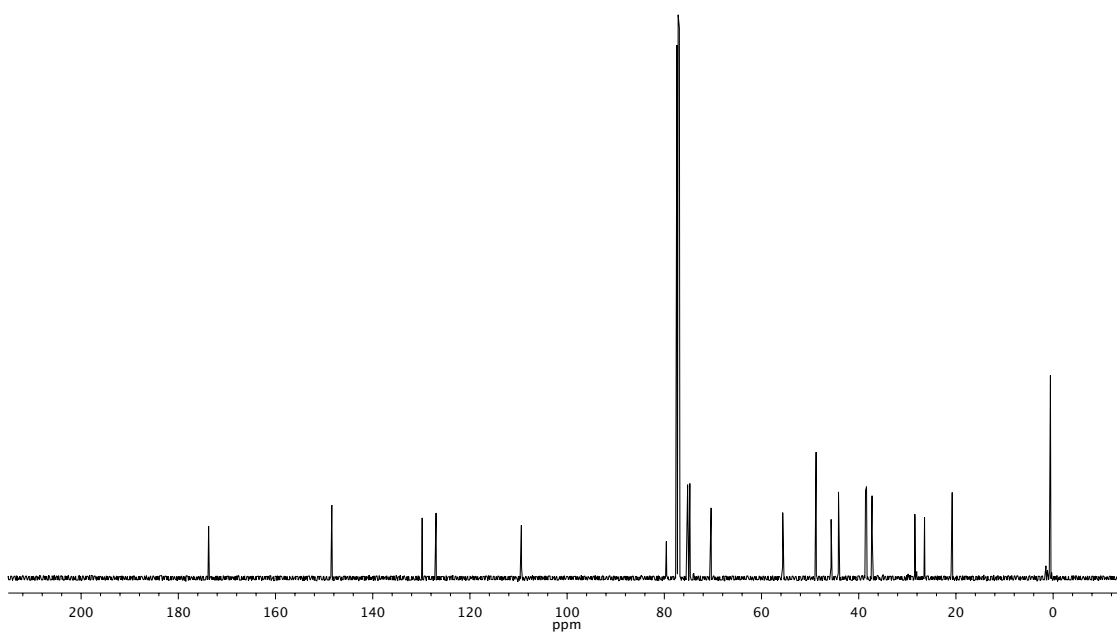


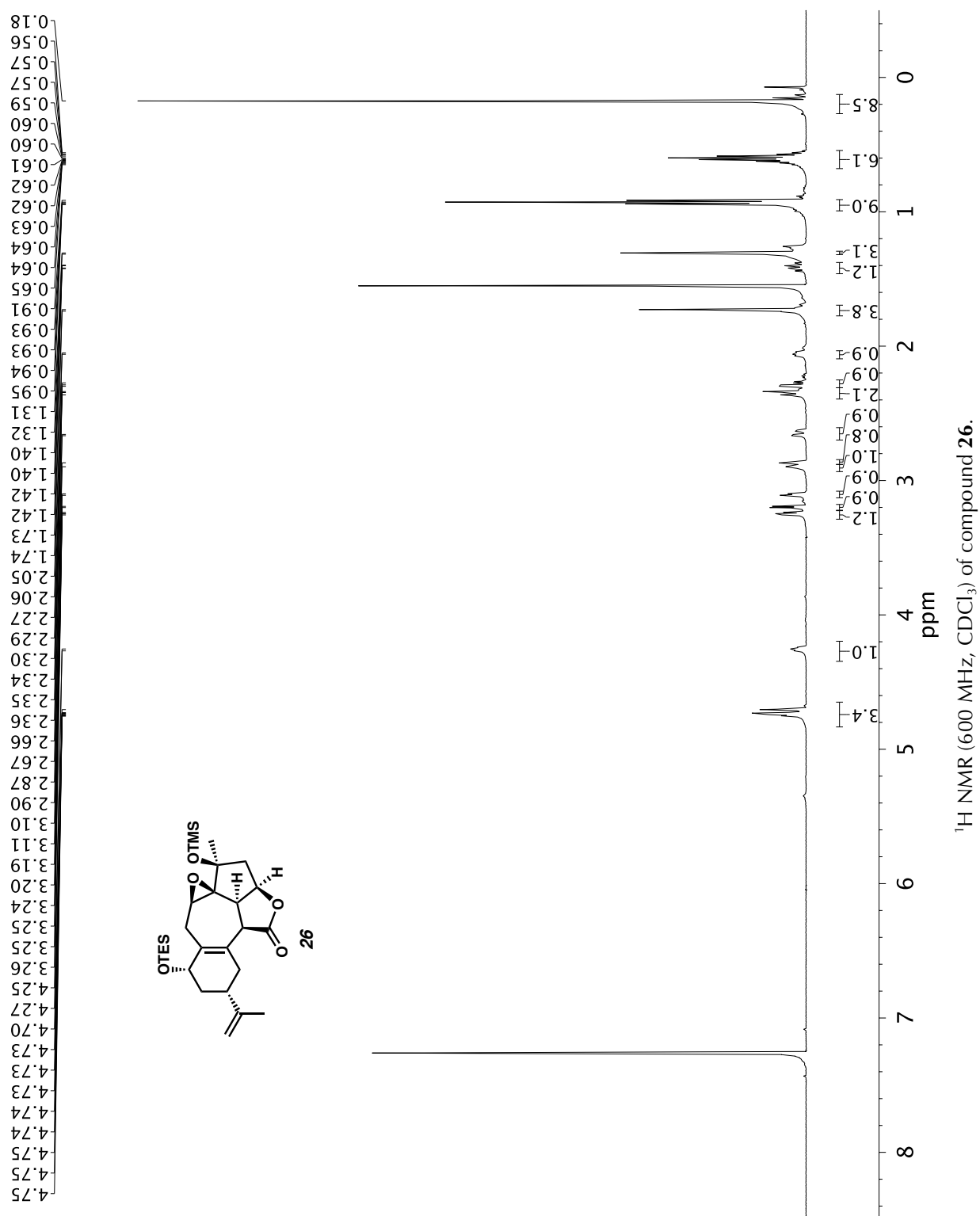
Infrared spectrum (Thin Film, NaCl) of compound **19**.¹³C NMR (101 MHz, CDCl₃) of compound **19**.

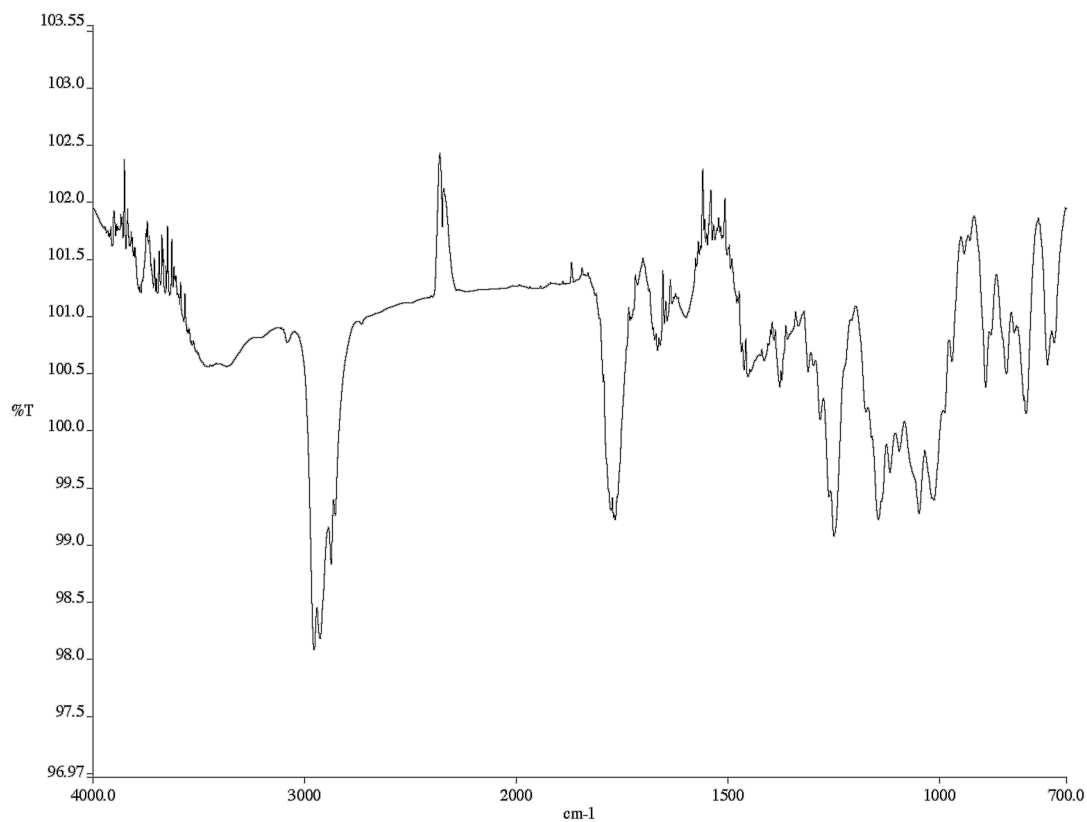
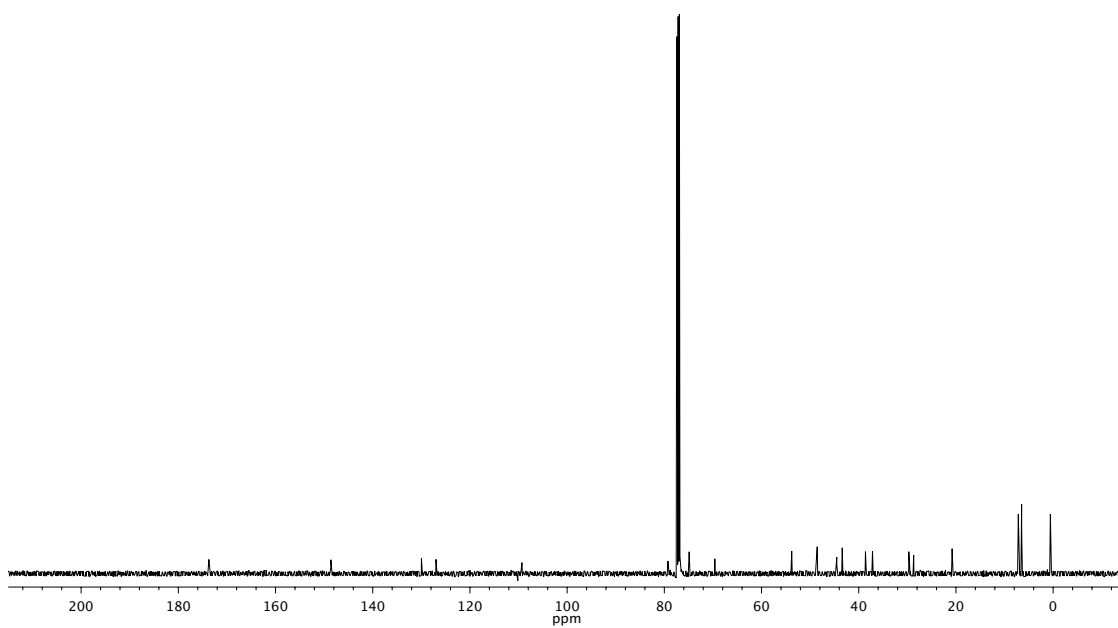


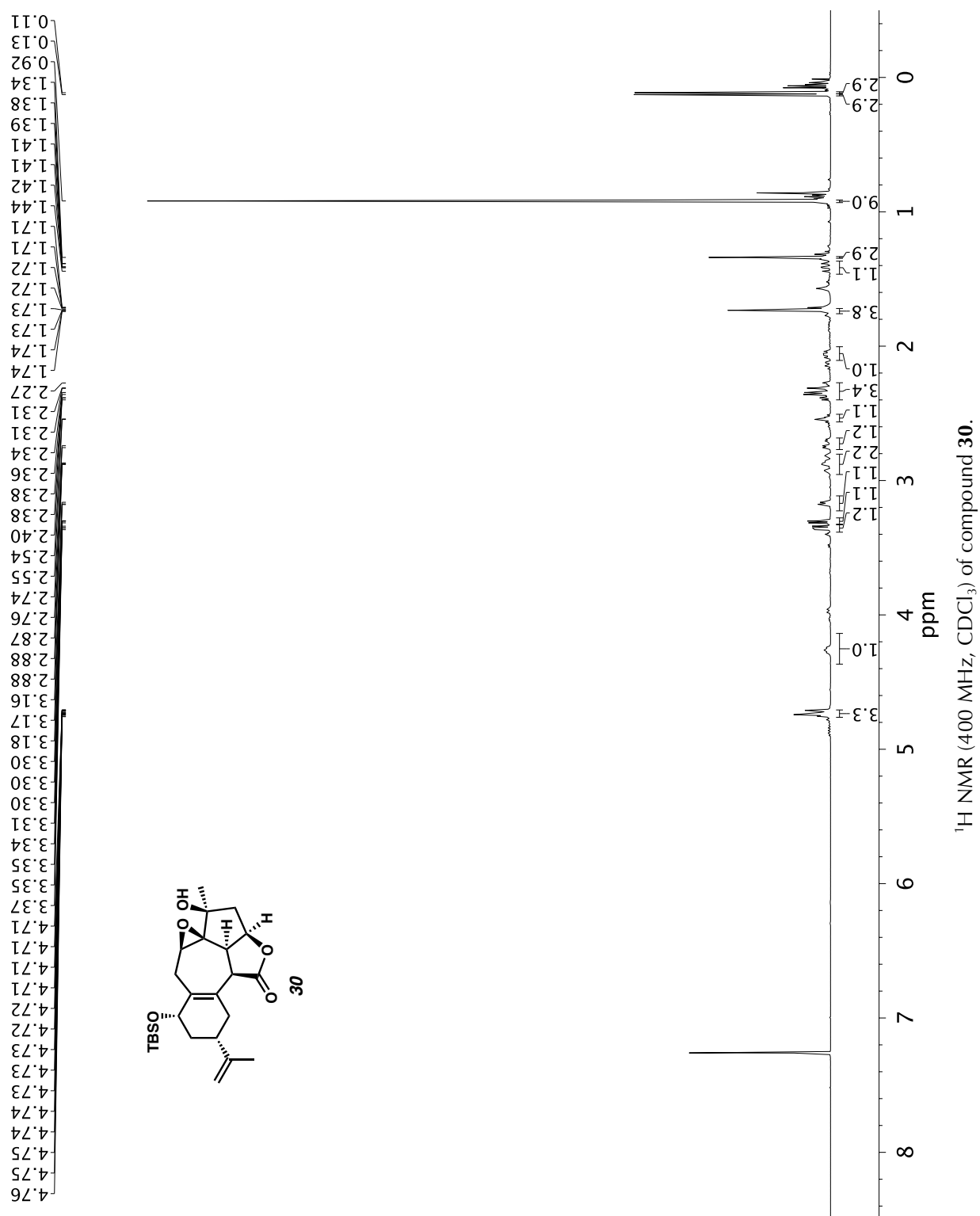
Infrared spectrum (Thin Film, NaCl) of compound **24**.¹³C NMR (126 MHz, CDCl₃) of compound **24**.

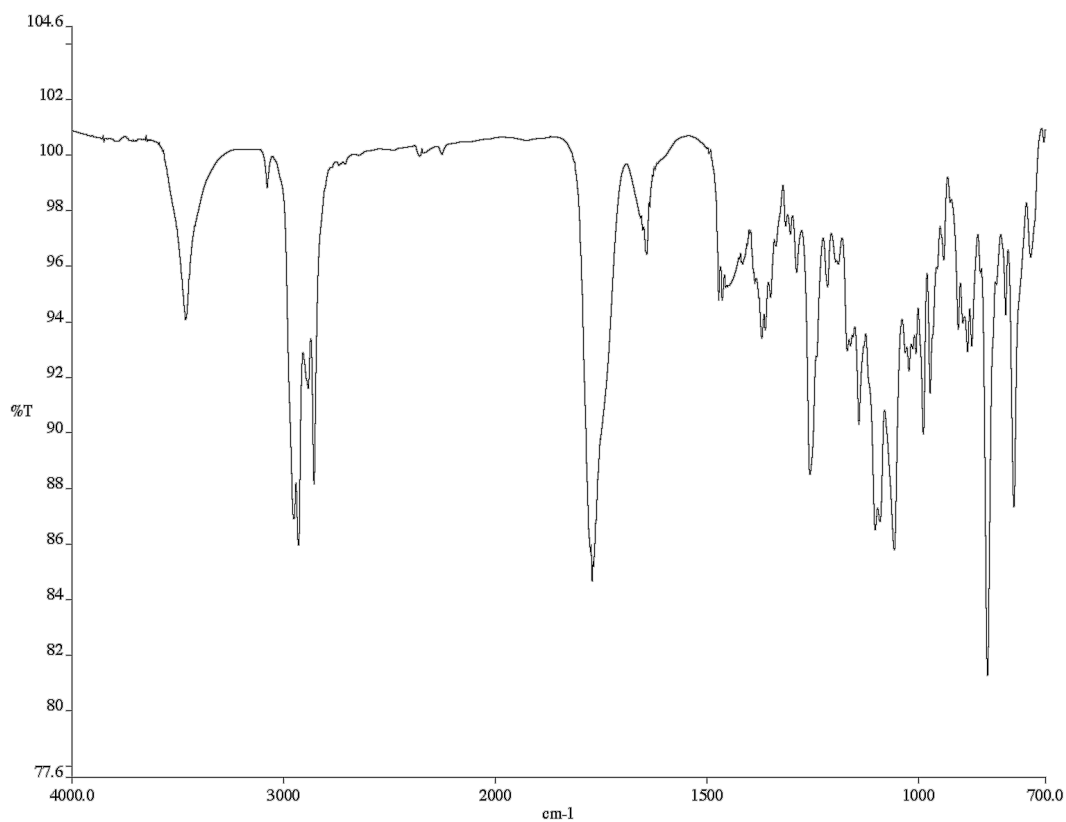
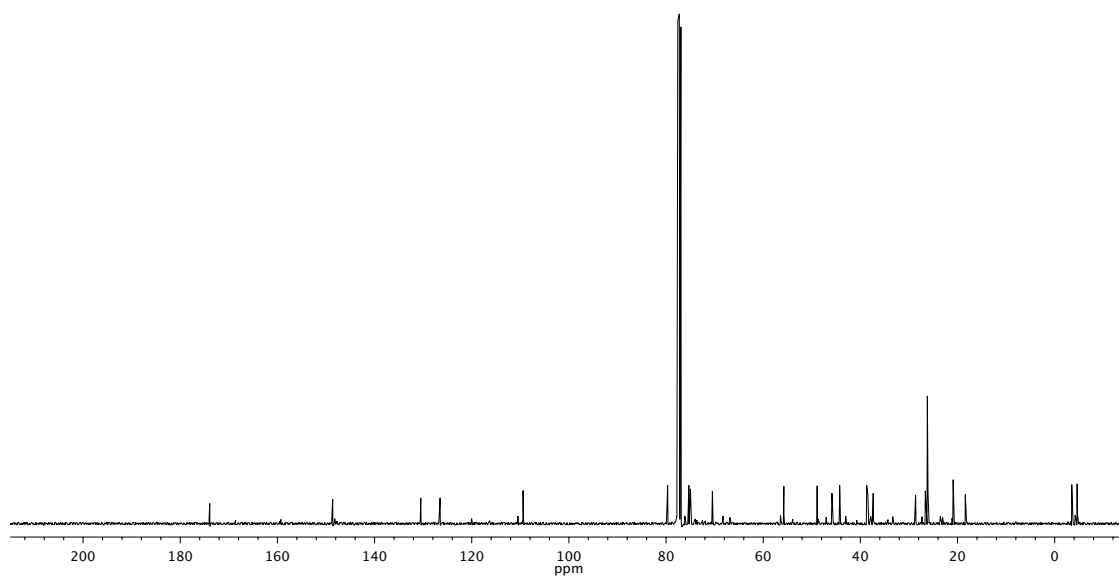


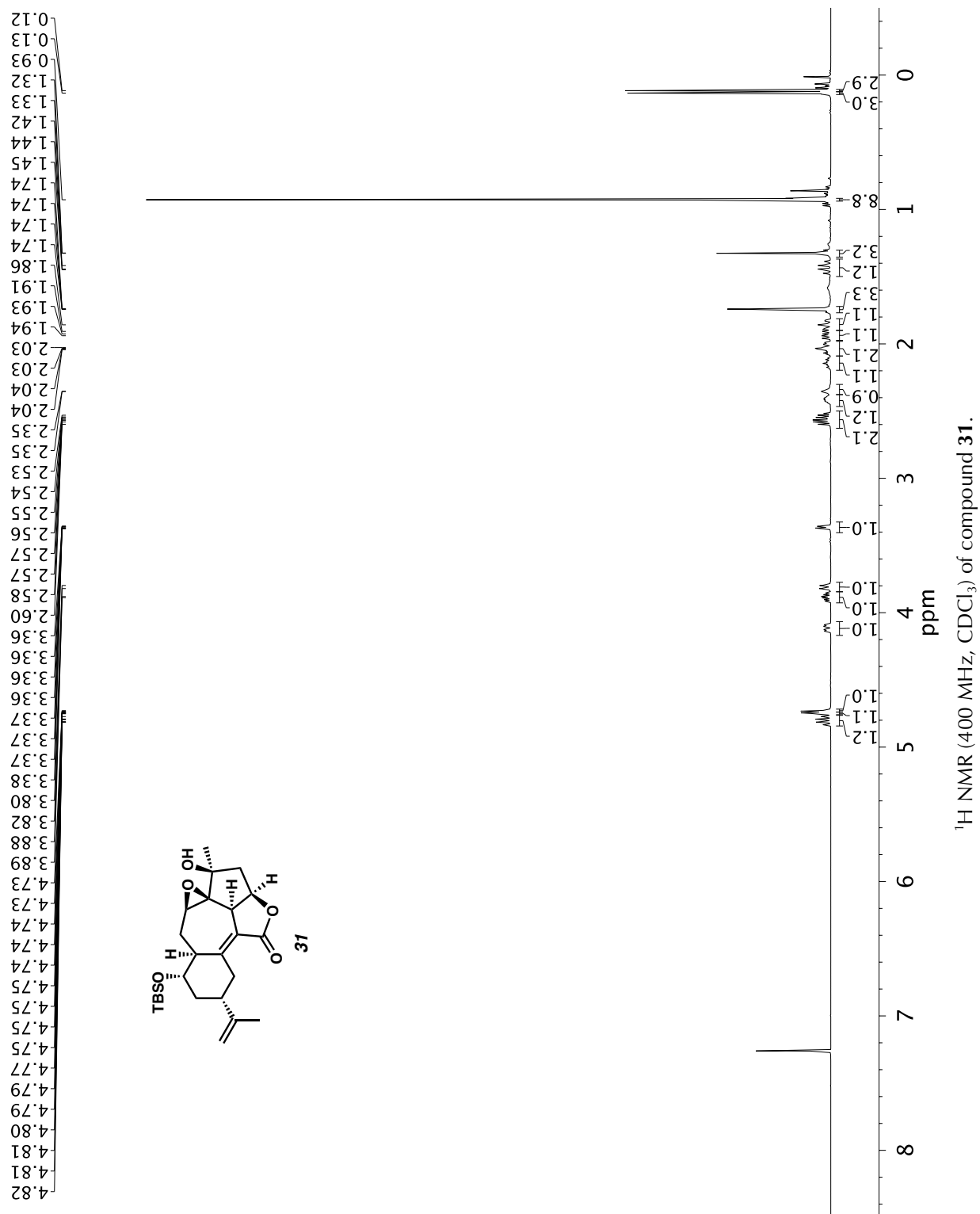
Infrared spectrum (Thin Film, NaCl) of compound **25**.¹³C NMR (126 MHz, CDCl₃) of compound **25**.

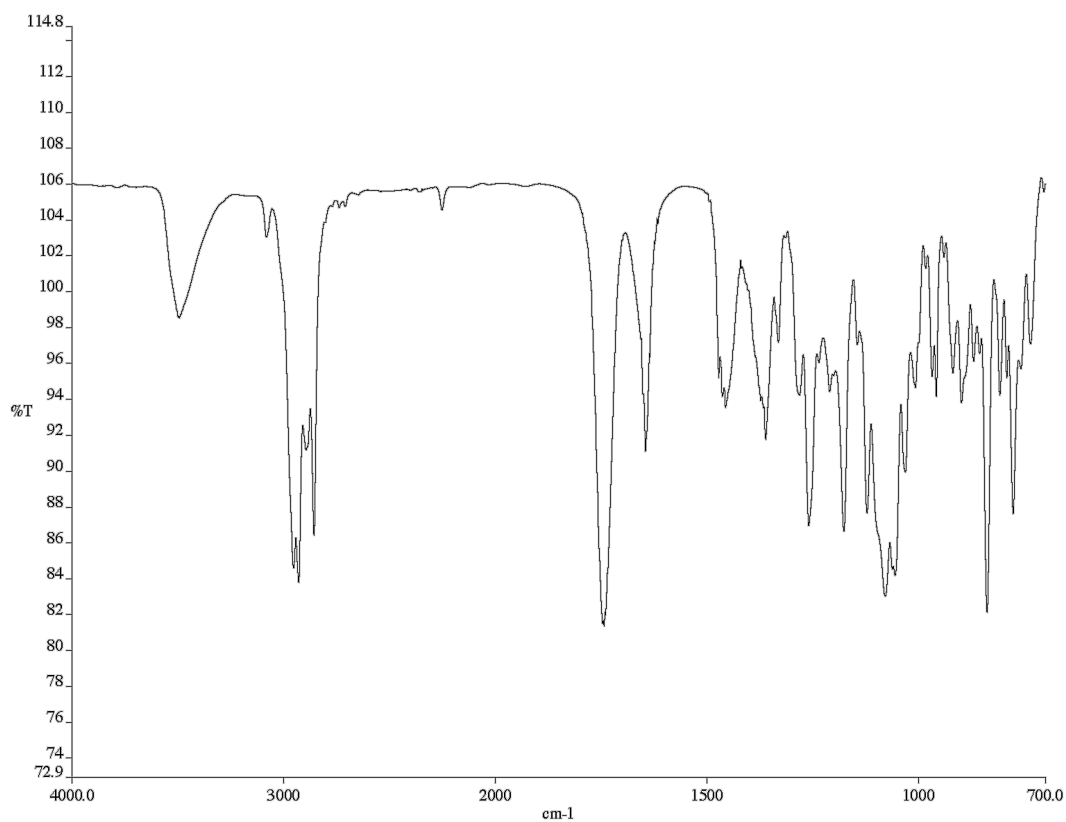
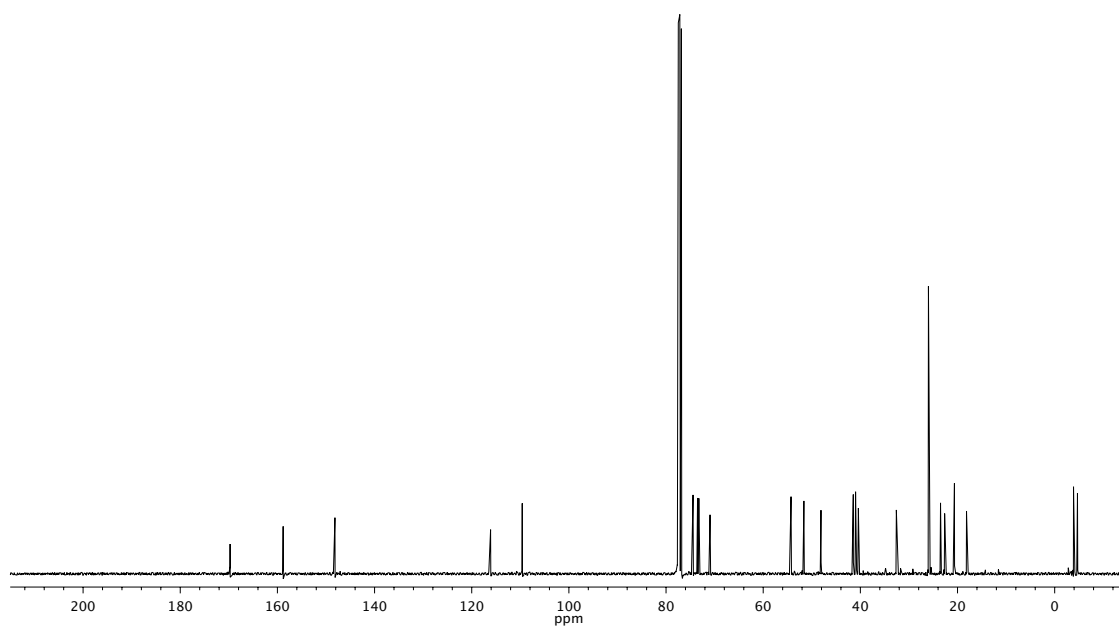


Infrared spectrum (Thin Film, NaCl) of compound **26**.¹³C NMR (126 MHz, CDCl₃) of compound **26**.

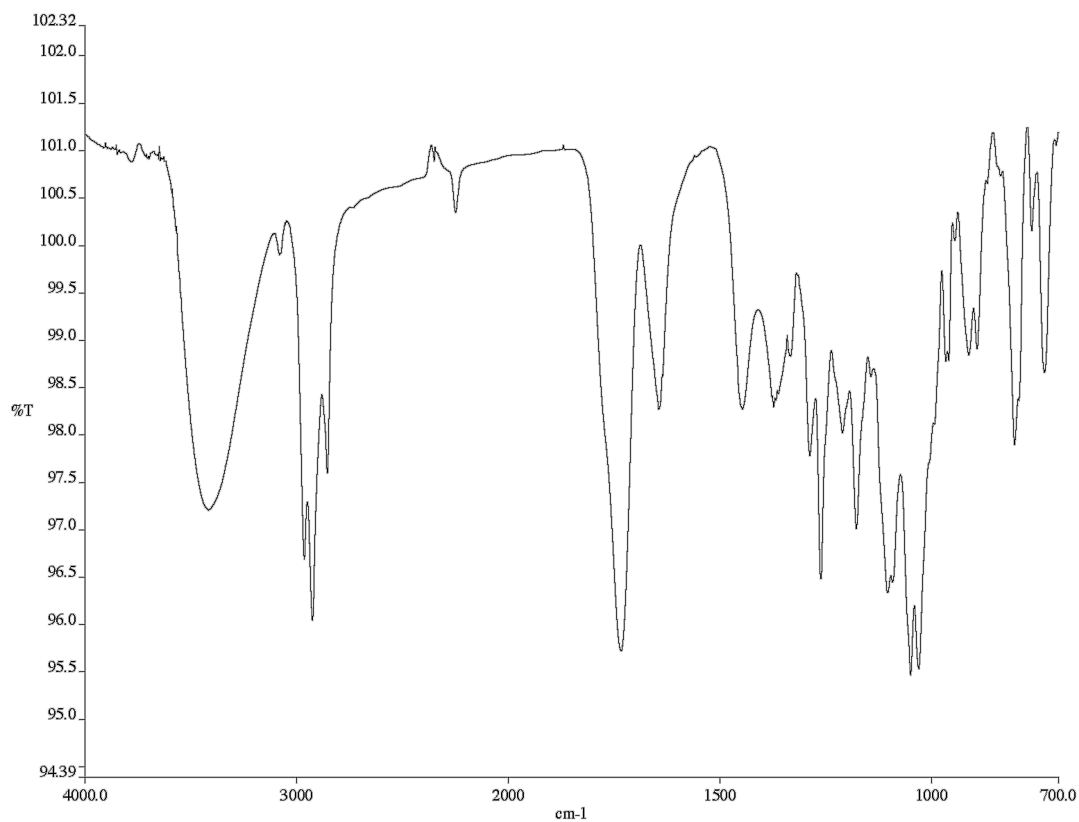
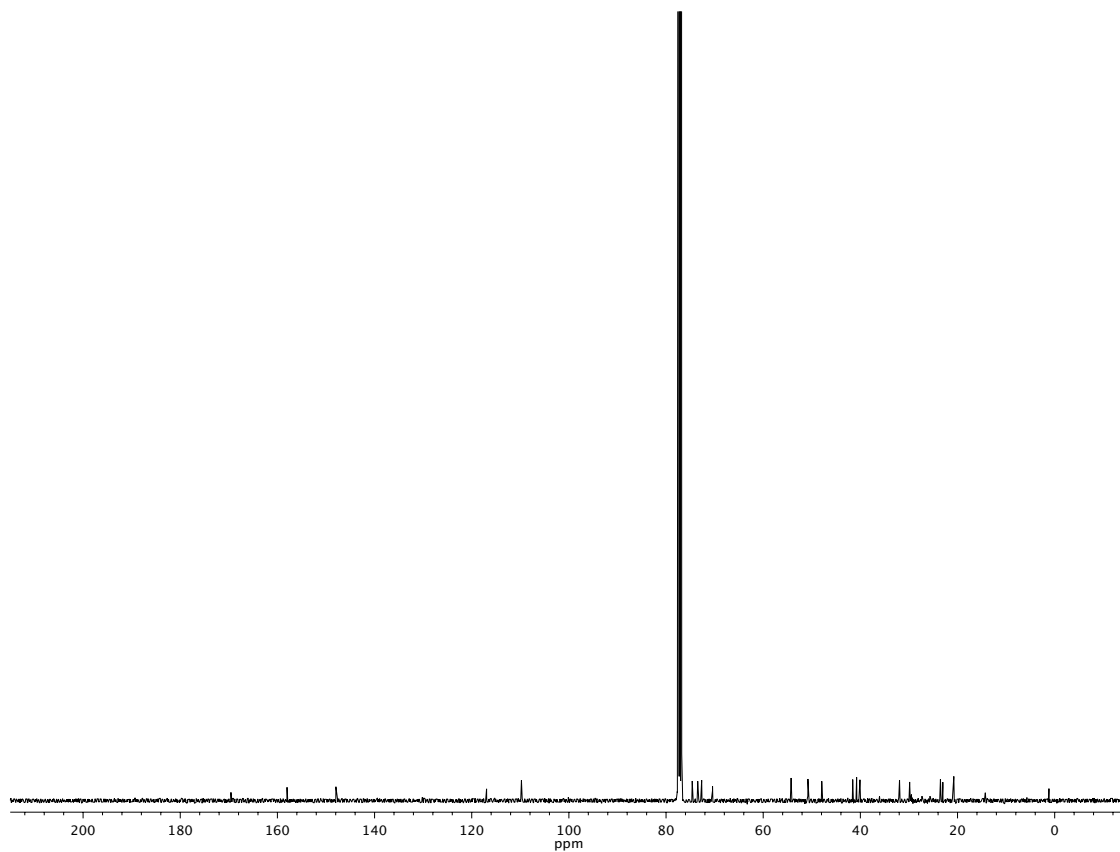


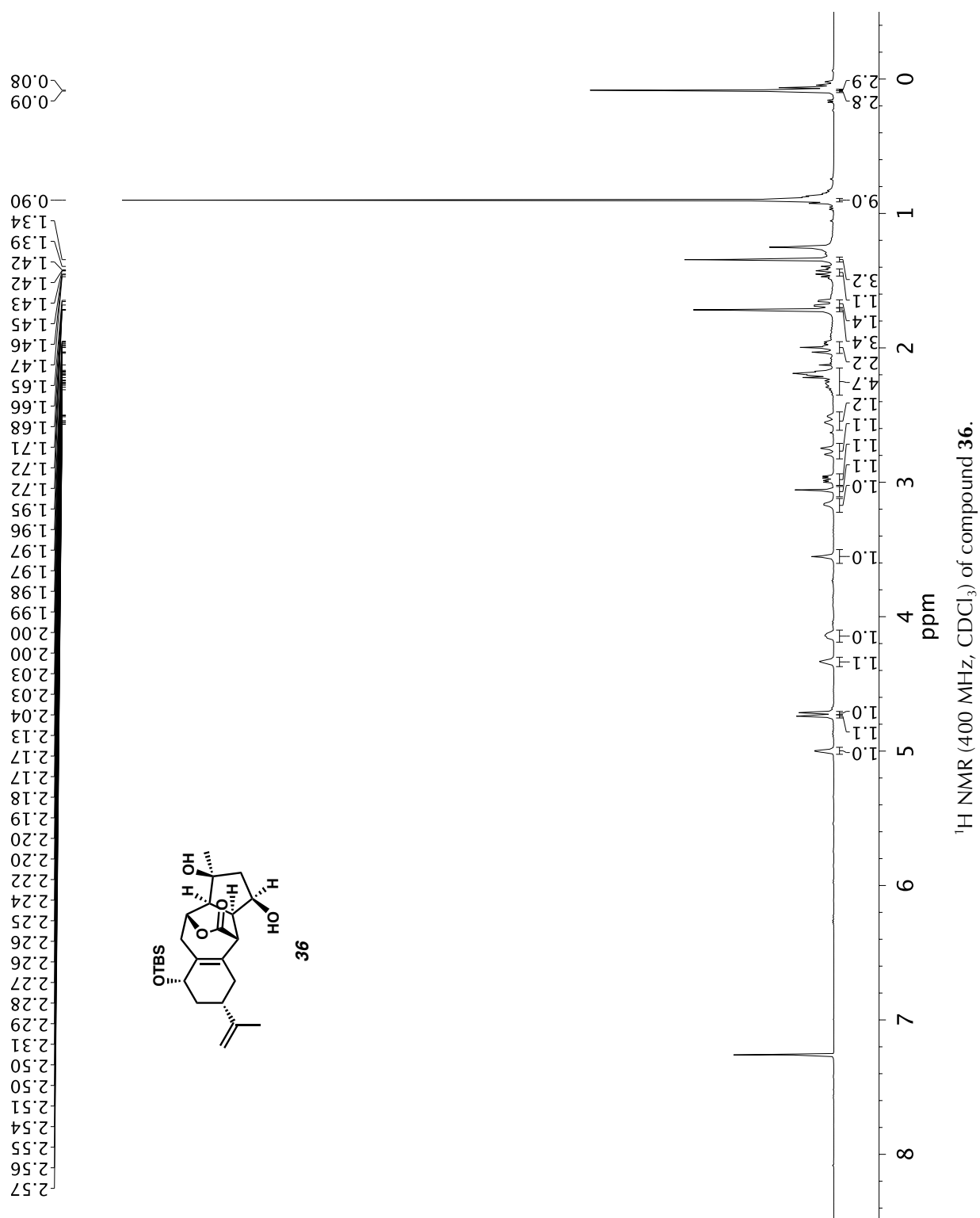
Infrared spectrum (Thin Film, NaCl) of compound **30**.¹³C NMR (101 MHz, CDCl₃) of compound **30**.

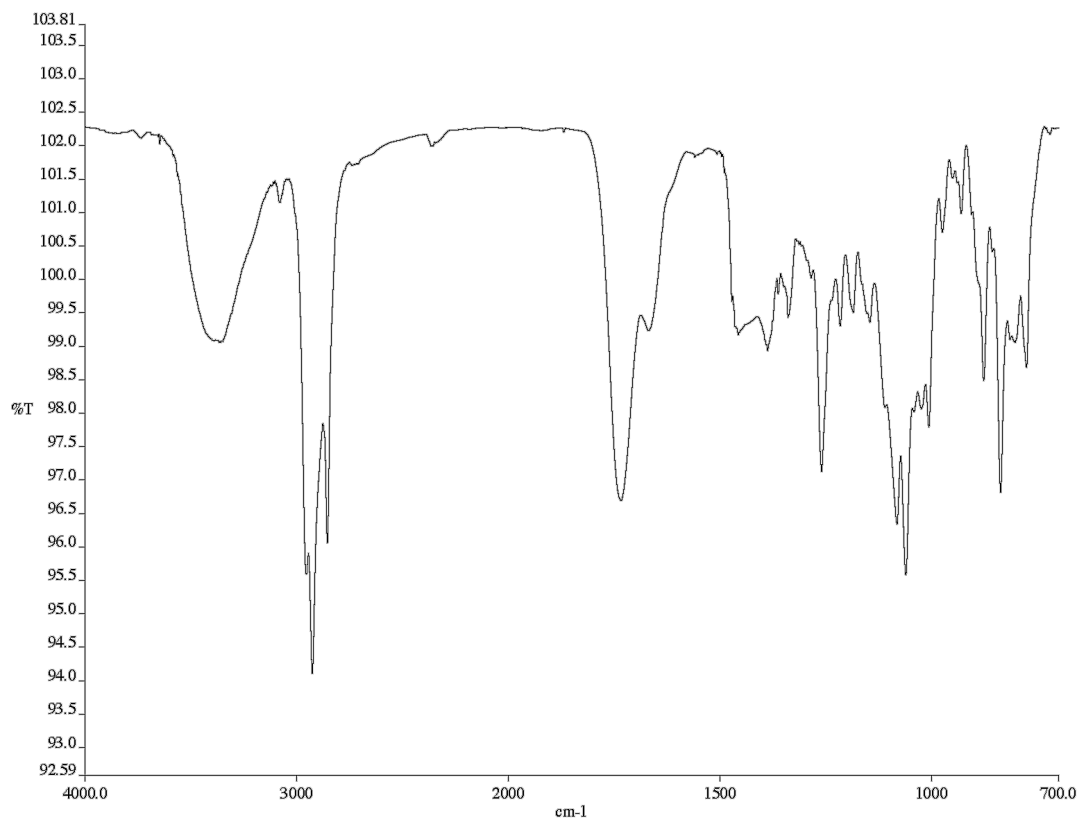
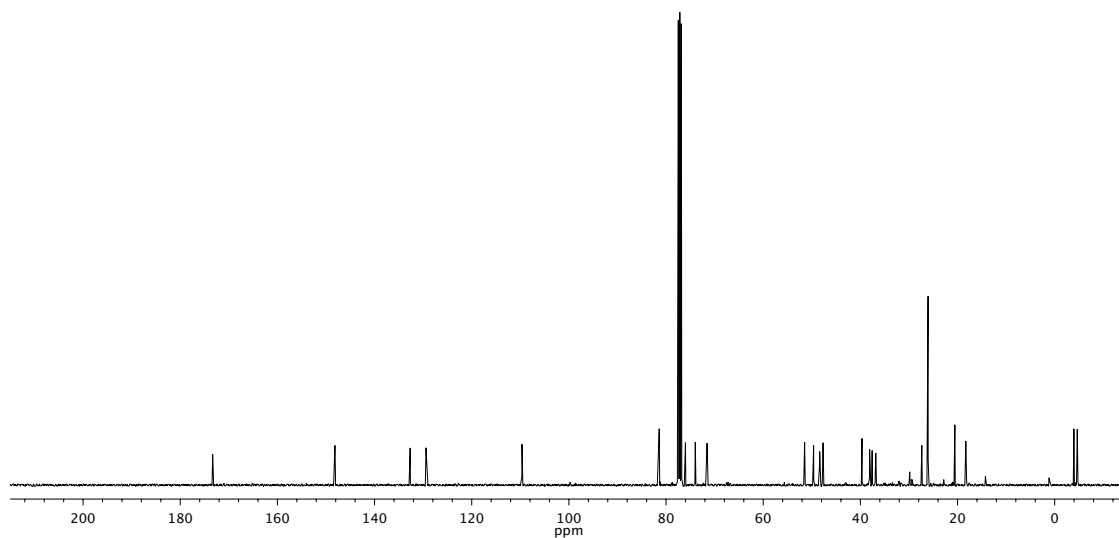


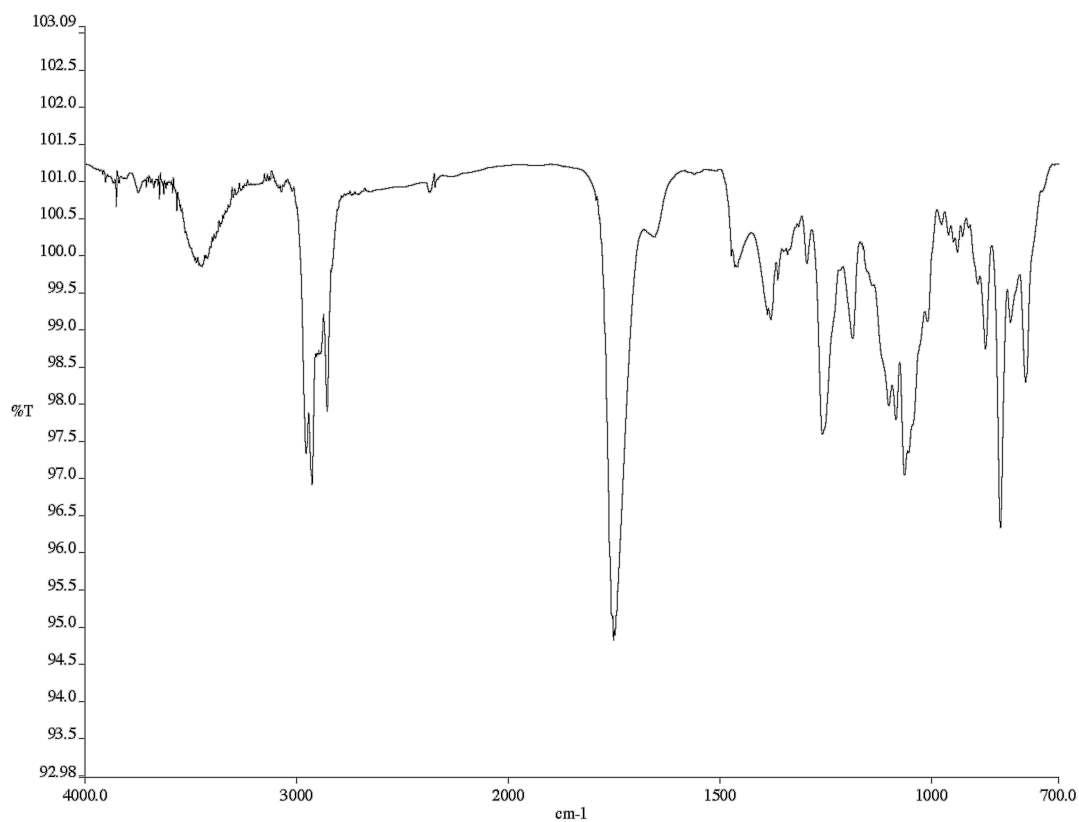
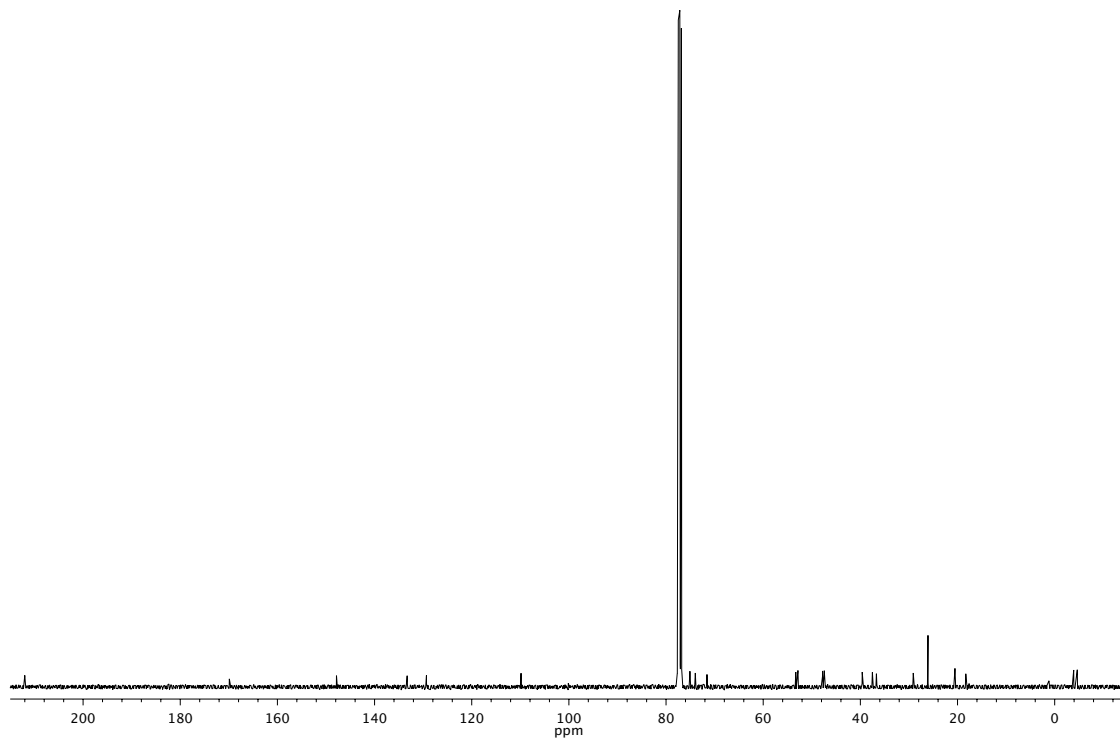
Infrared spectrum (Thin Film, NaCl) of compound **31**.¹³C NMR (101 MHz, CDCl₃) of compound **31**.

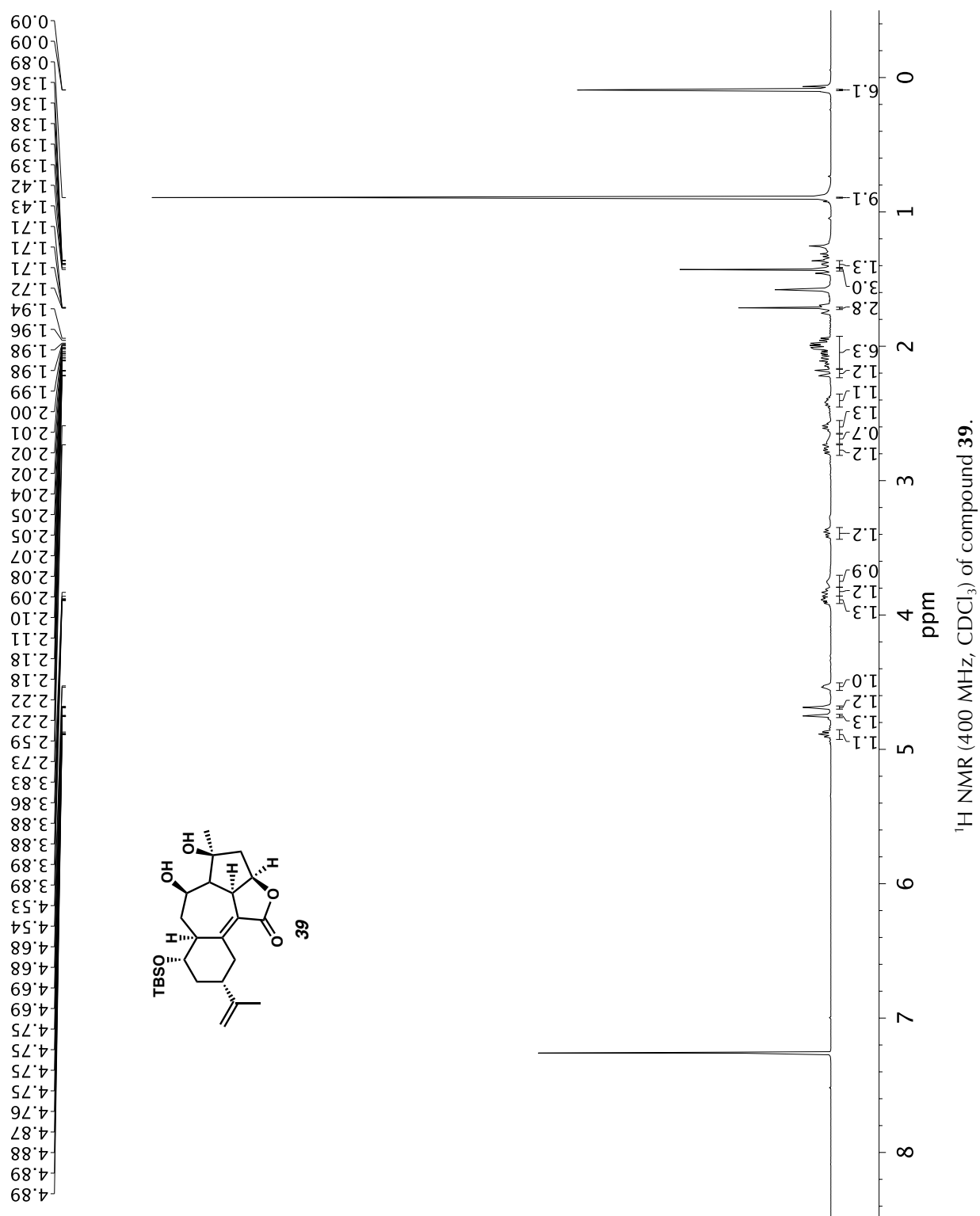


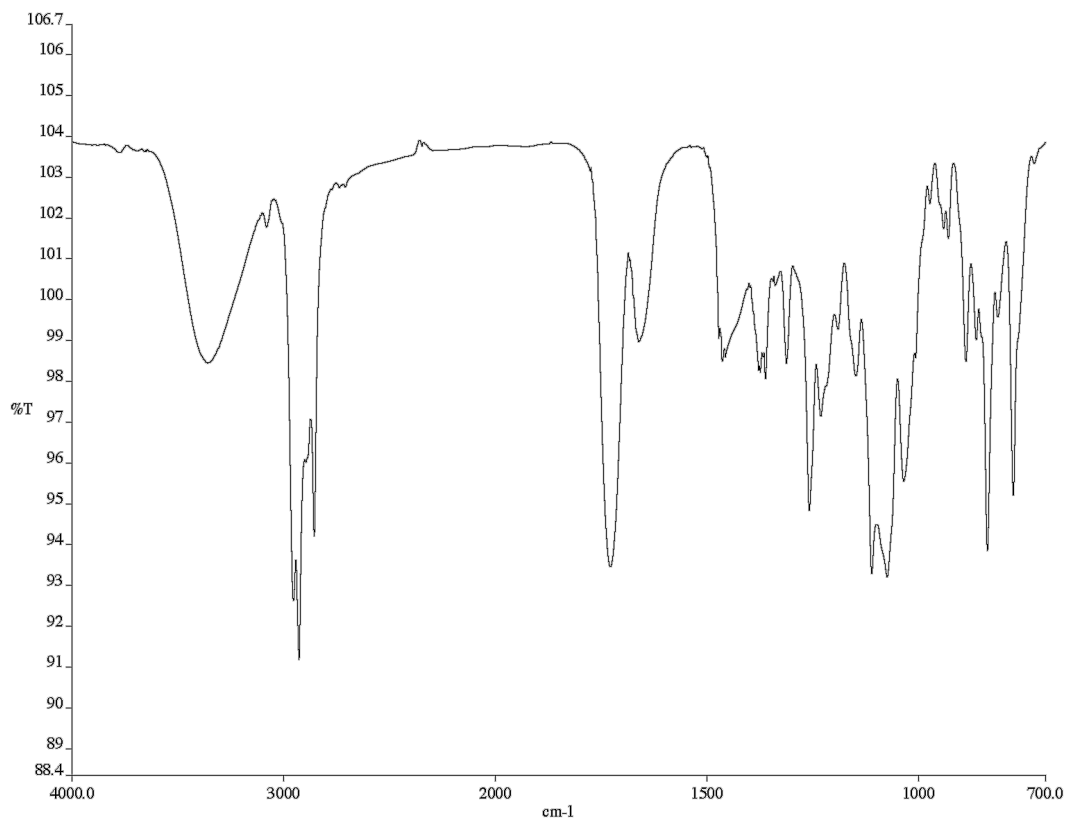
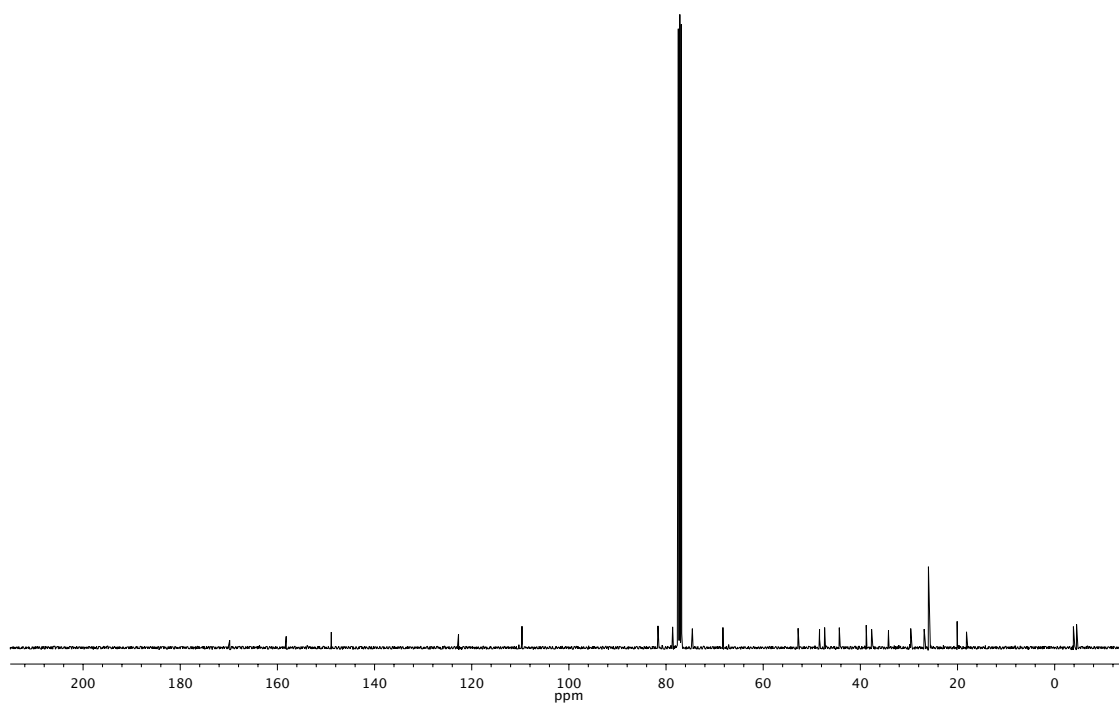
Infrared spectrum (Thin Film, NaCl) of compound **32**.¹³C NMR (101 MHz, CDCl₃) of compound **32**.

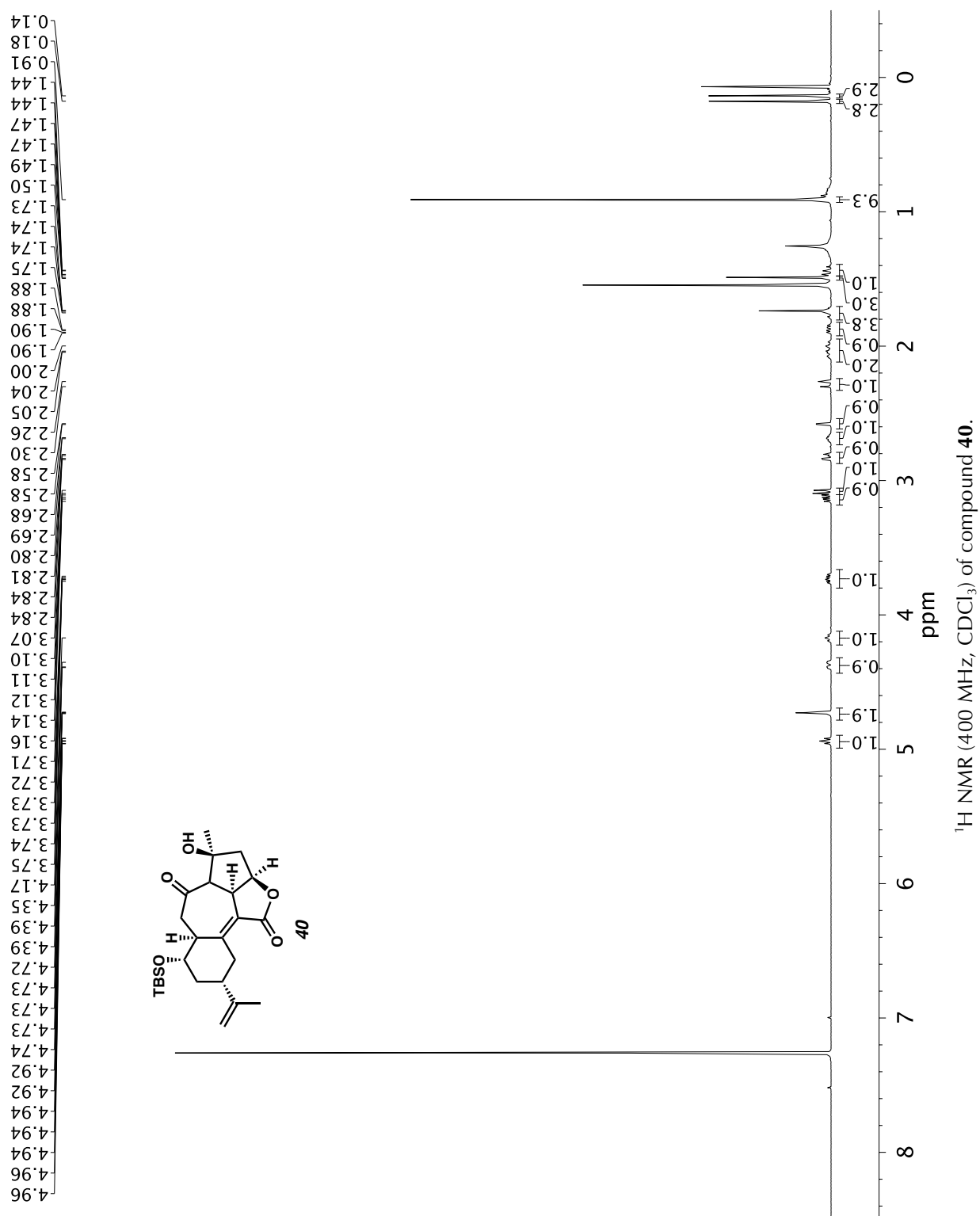


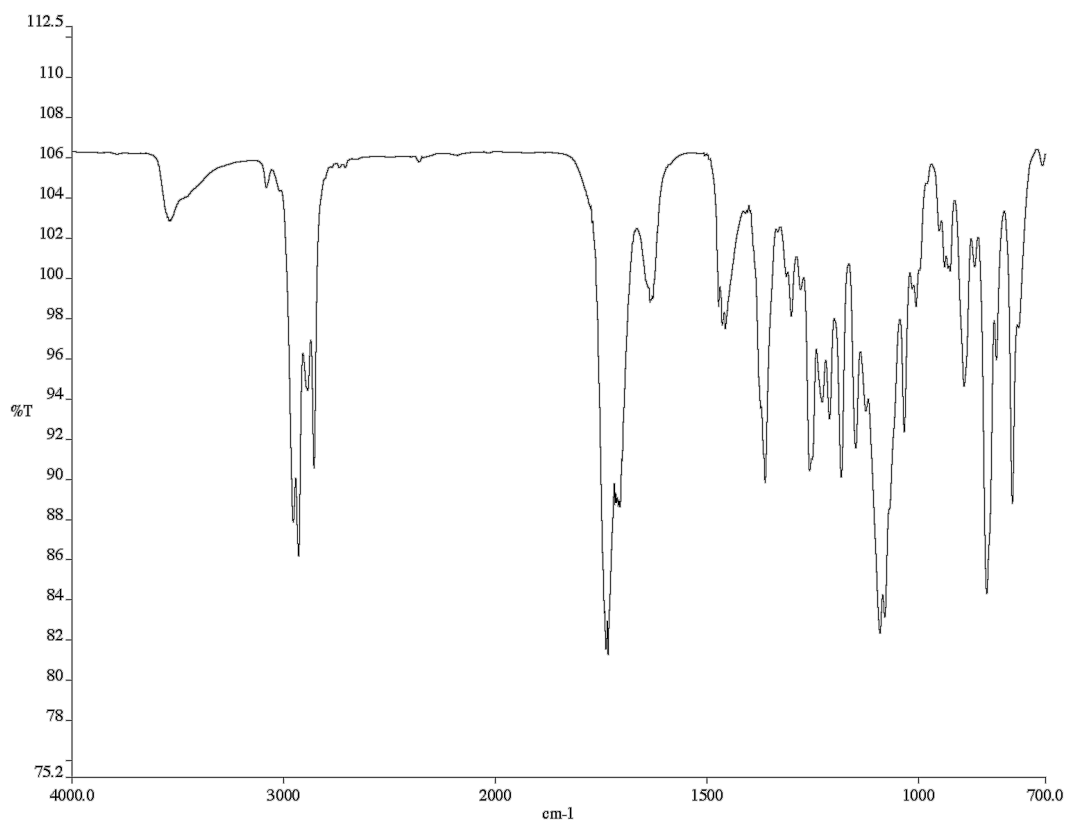
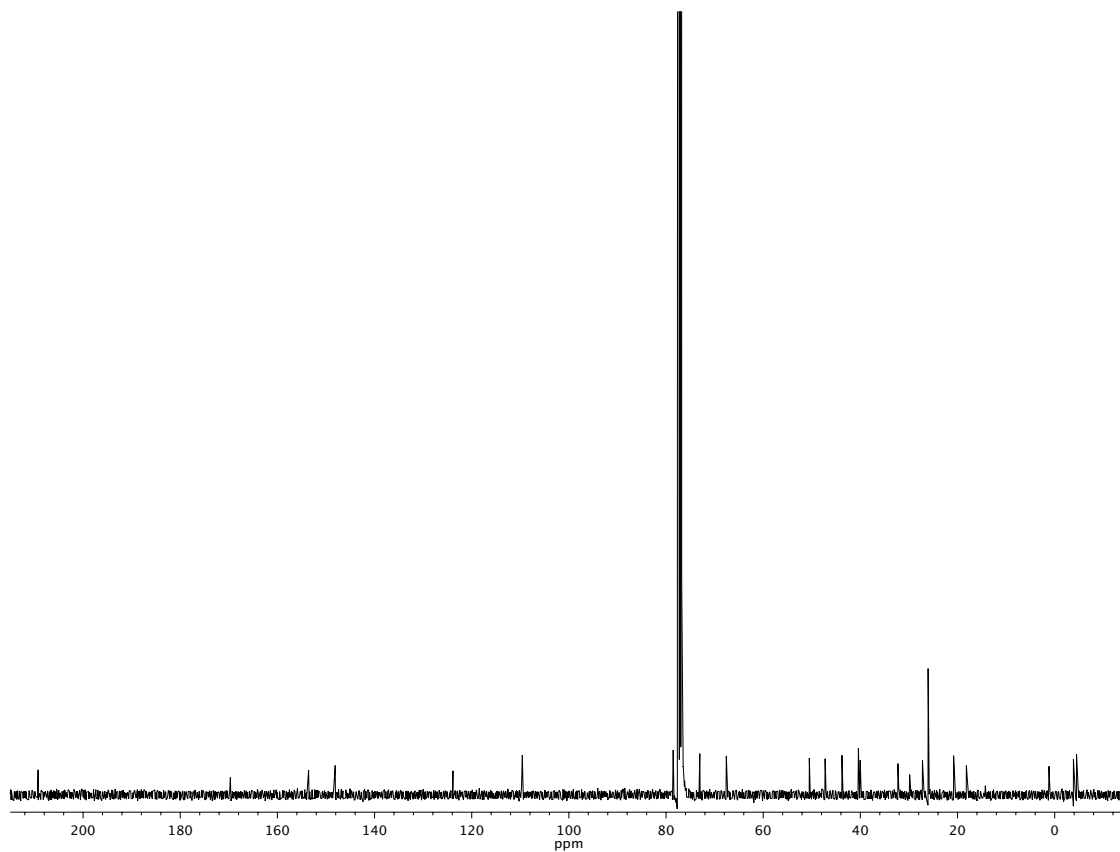
Infrared spectrum (Thin Film, NaCl) of compound **36**.¹³C NMR (101 MHz, CDCl₃) of compound **36**.

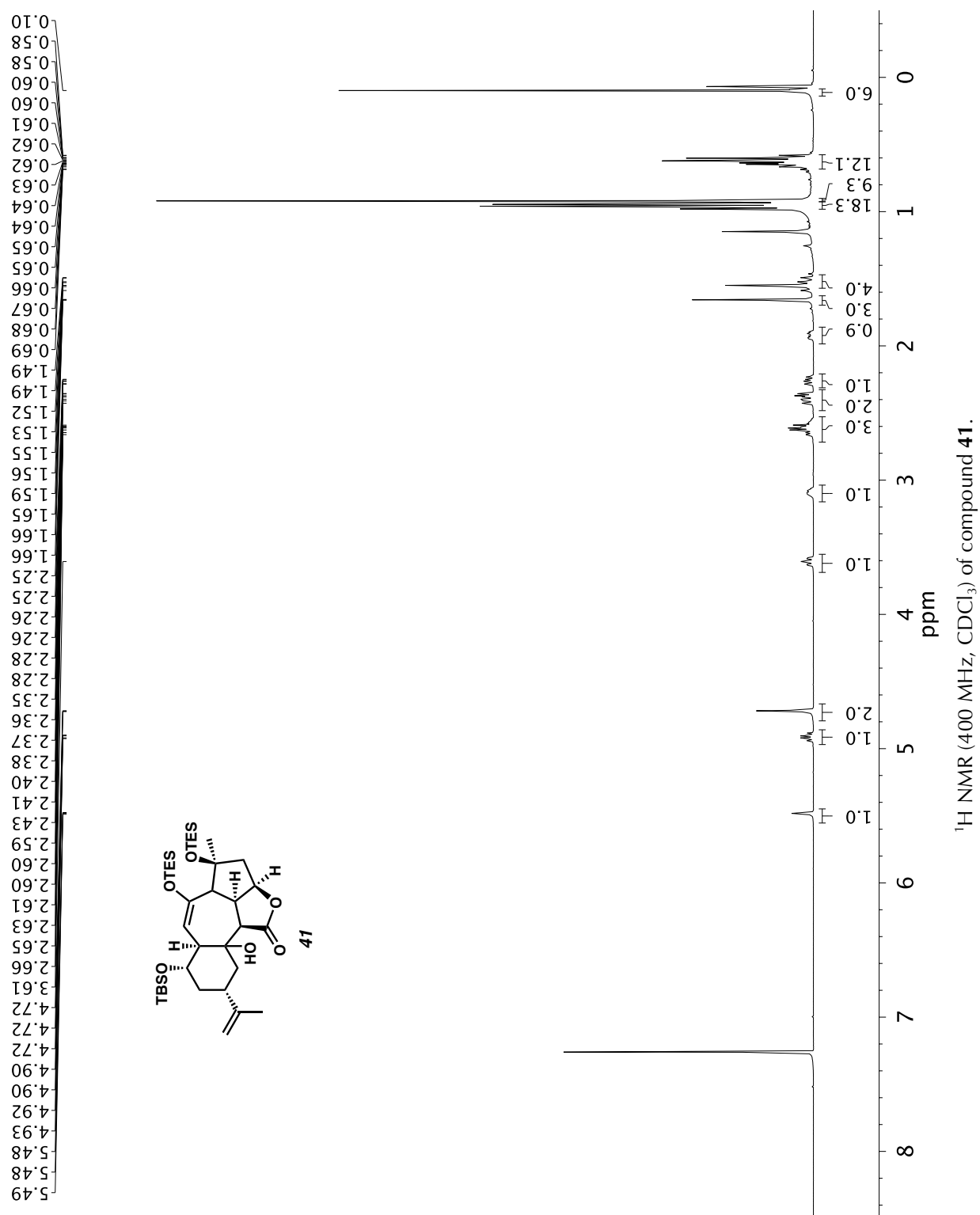
Infrared spectrum (Thin Film, NaCl) of compound **37**.¹³C NMR (101 MHz, CDCl₃) of compound **37**.

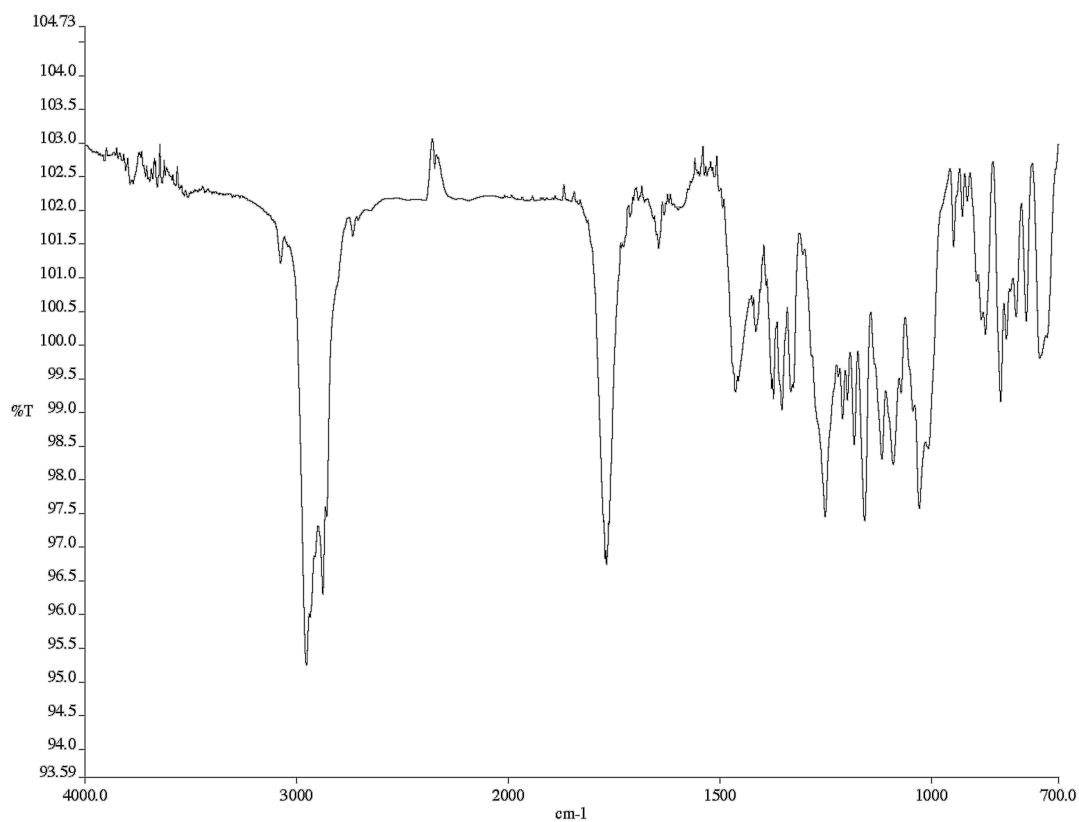
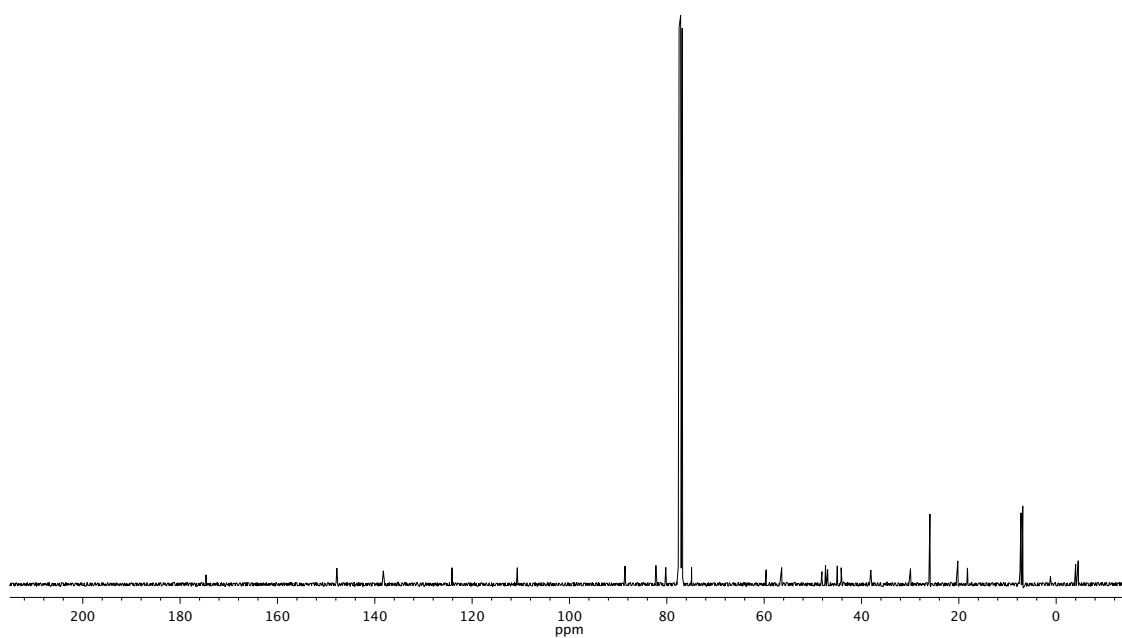


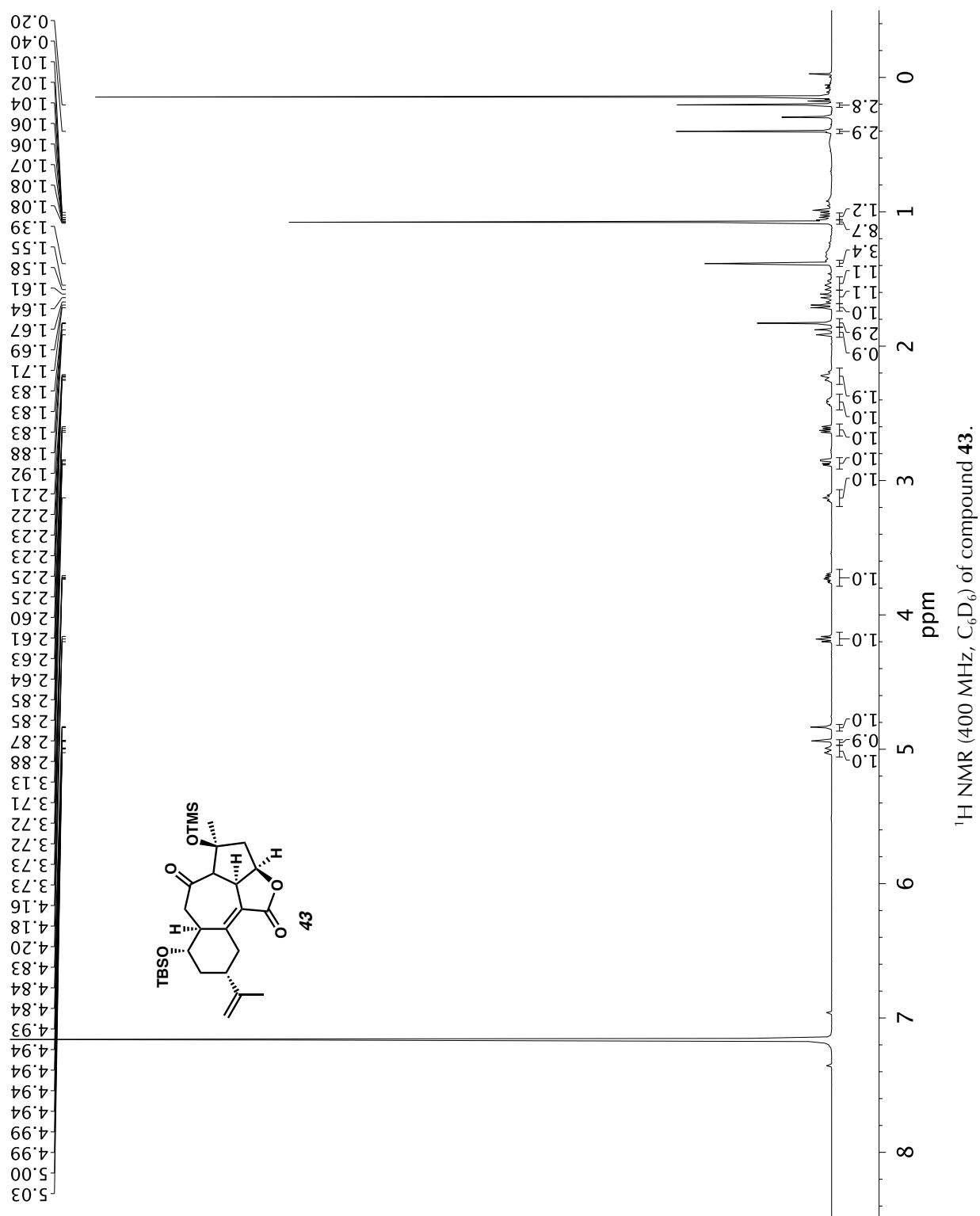
Infrared spectrum (Thin Film, NaCl) of compound **39**.¹³C NMR (101 MHz, CDCl₃) of compound **39**.

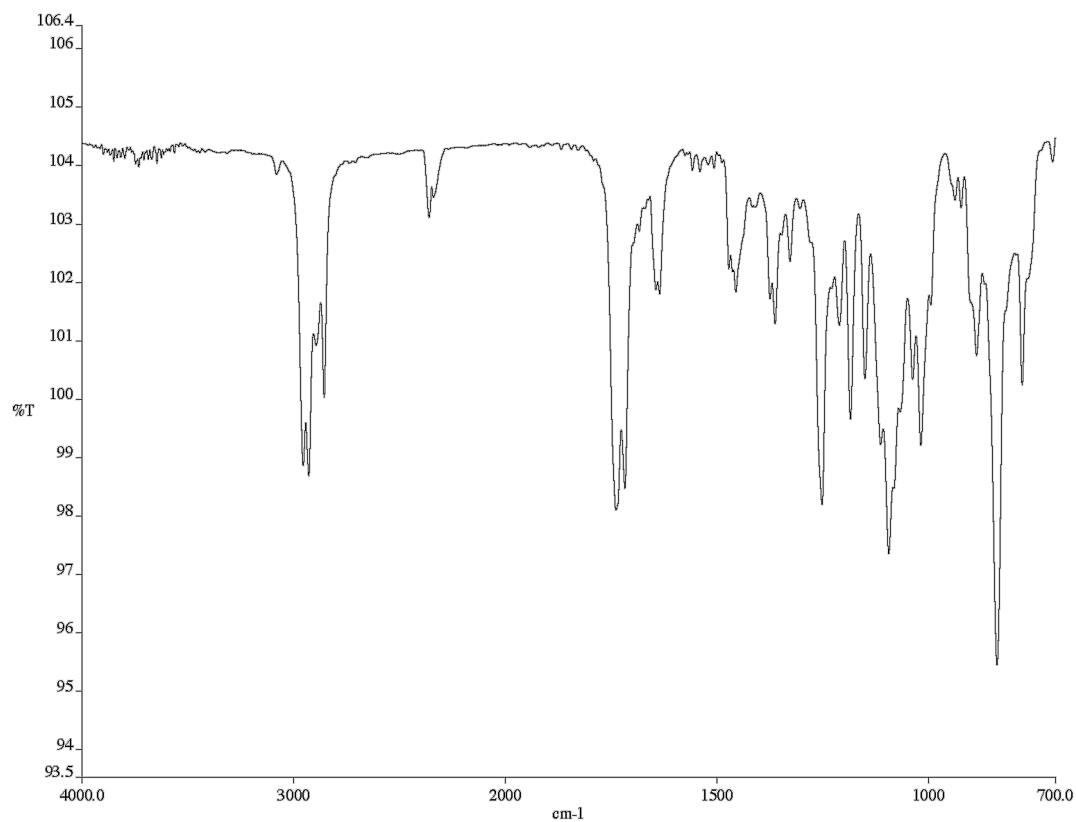
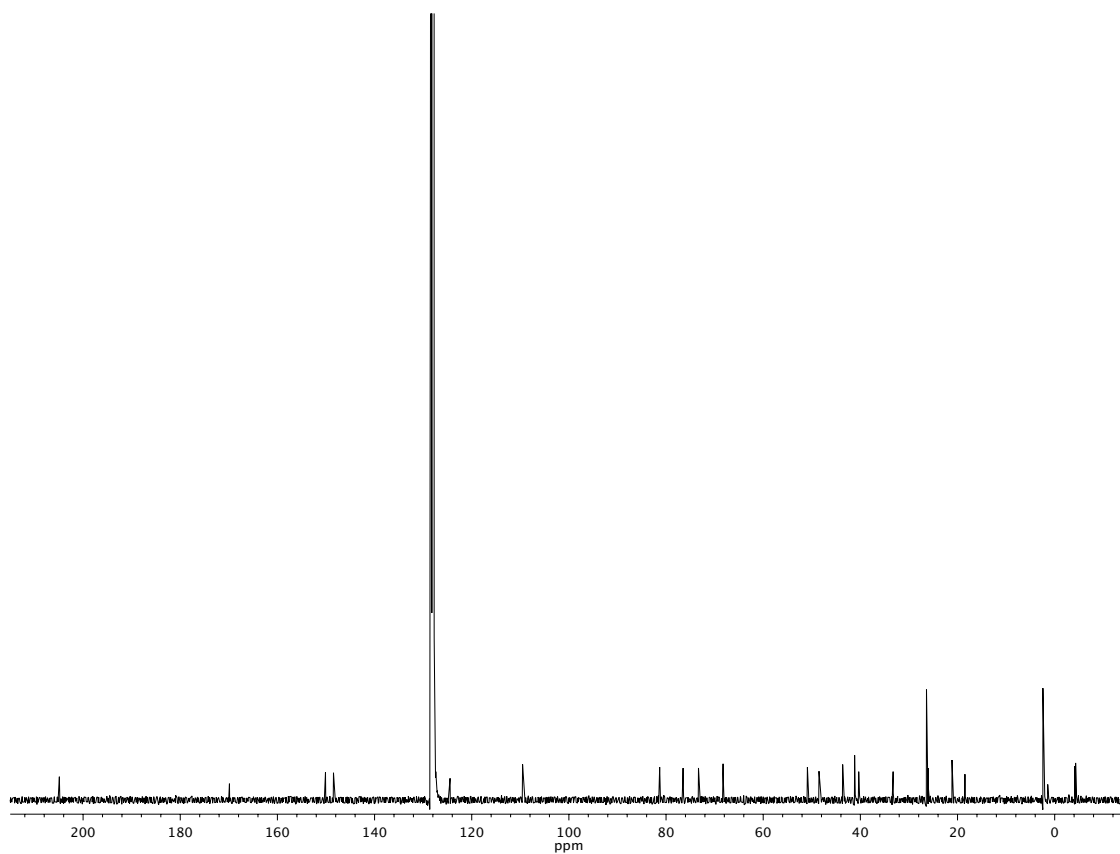


Infrared spectrum (Thin Film, NaCl) of compound **40**.¹³C NMR (101 MHz, CDCl₃) of compound **40**.

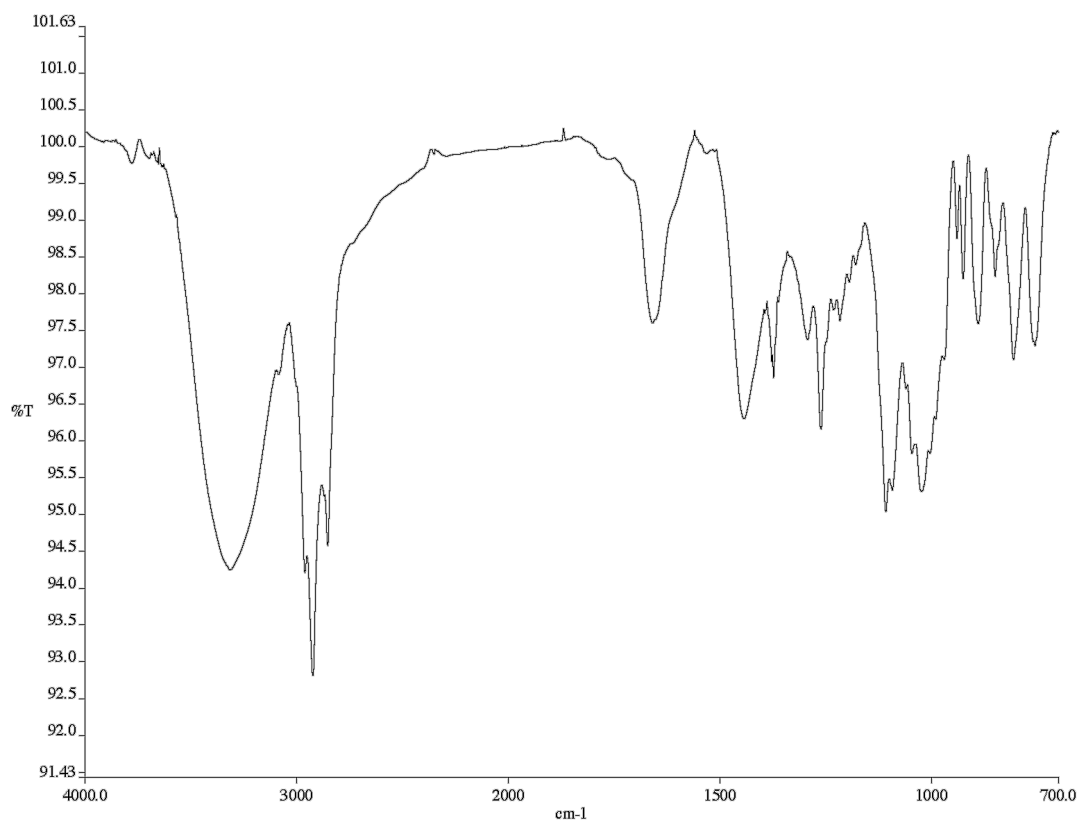
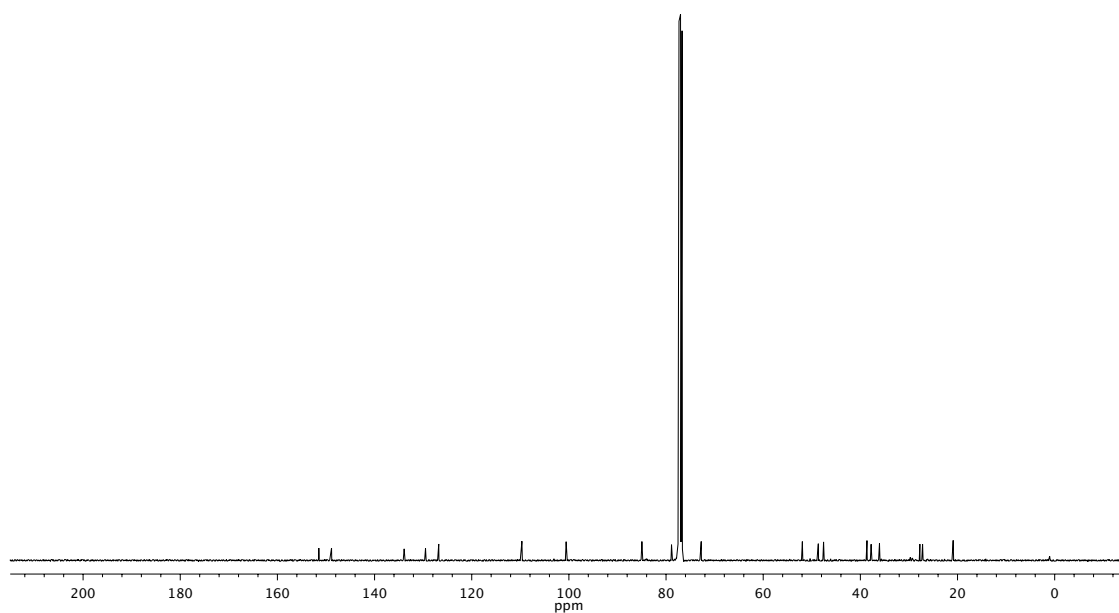


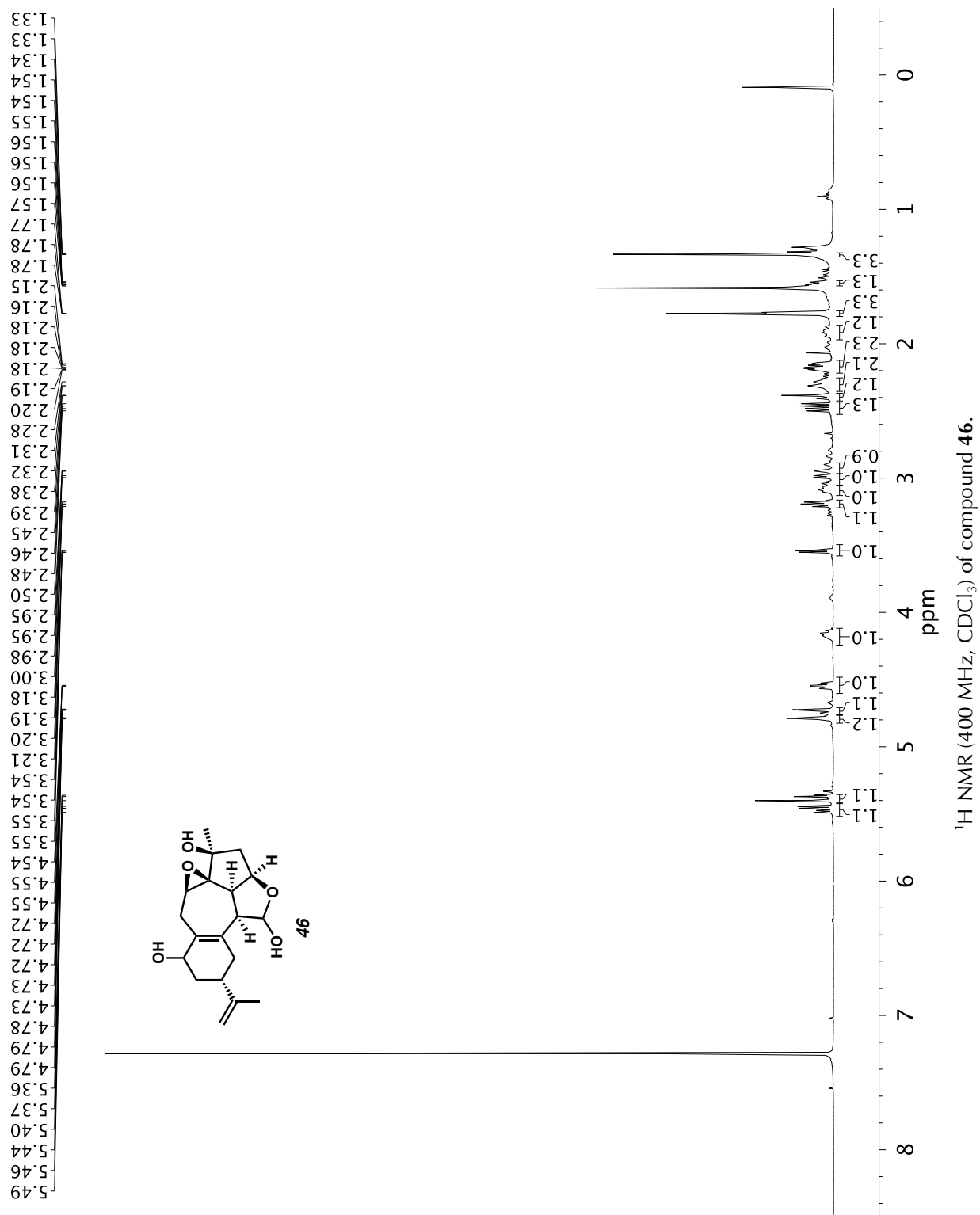
Infrared spectrum (Thin Film, NaCl) of compound **41**.¹³C NMR (101 MHz, CDCl₃) of compound **41**.

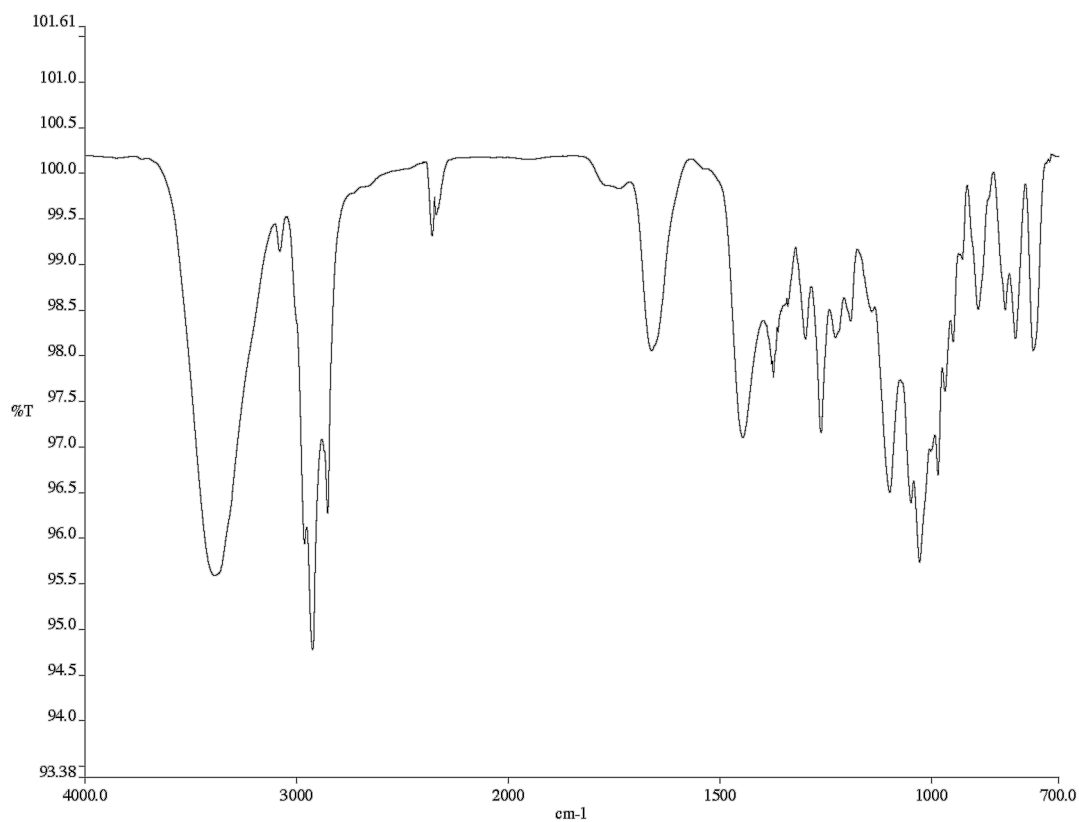
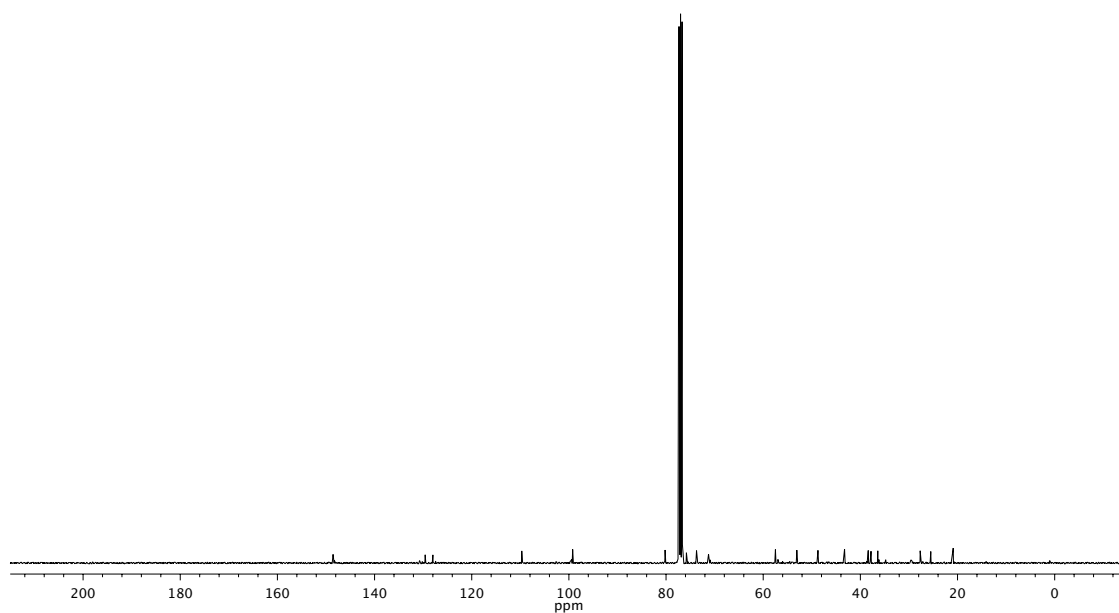


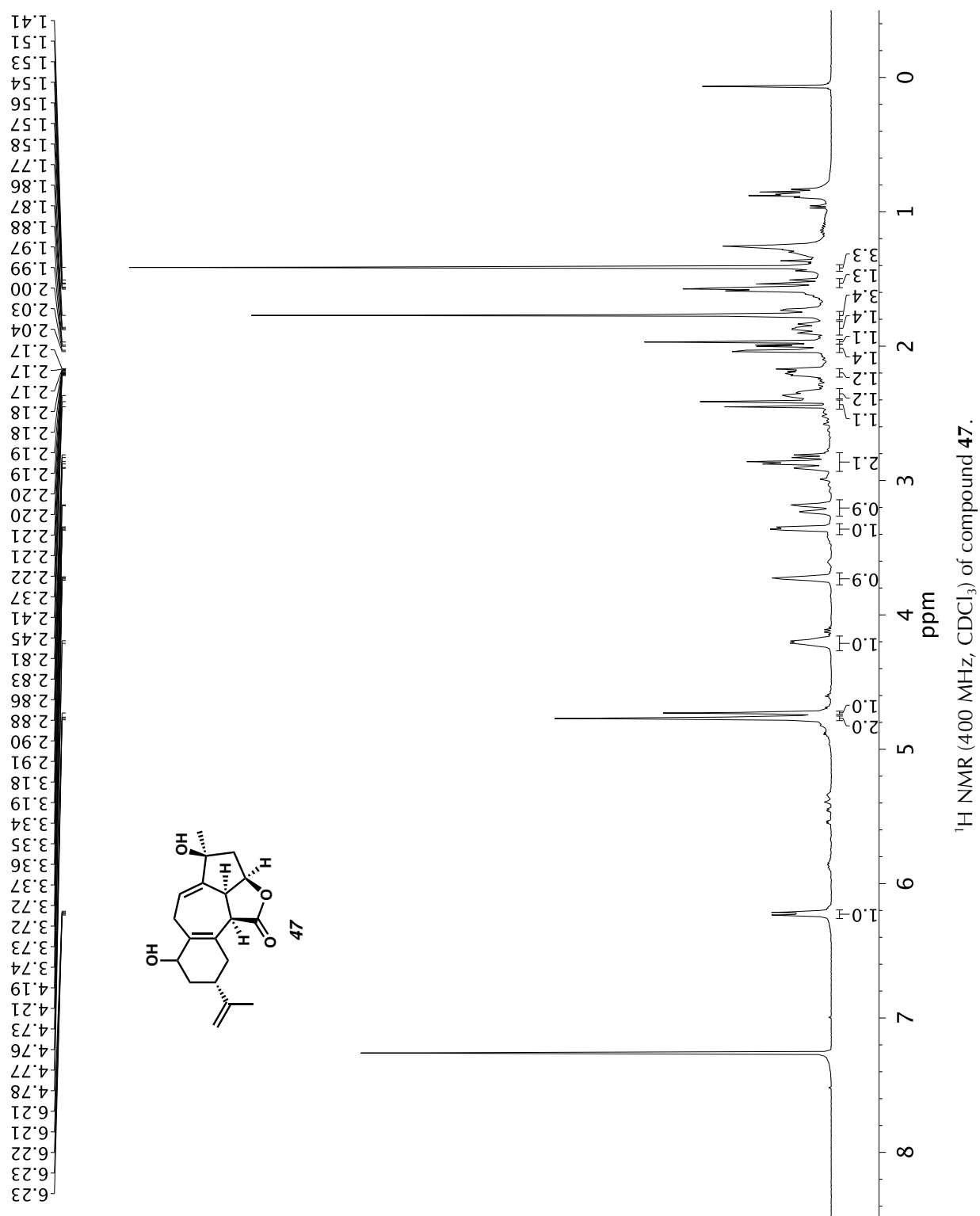
Infrared spectrum (Thin Film, NaCl) of compound **43**.¹³C NMR (101 MHz, C₆D₆) of compound **43**.

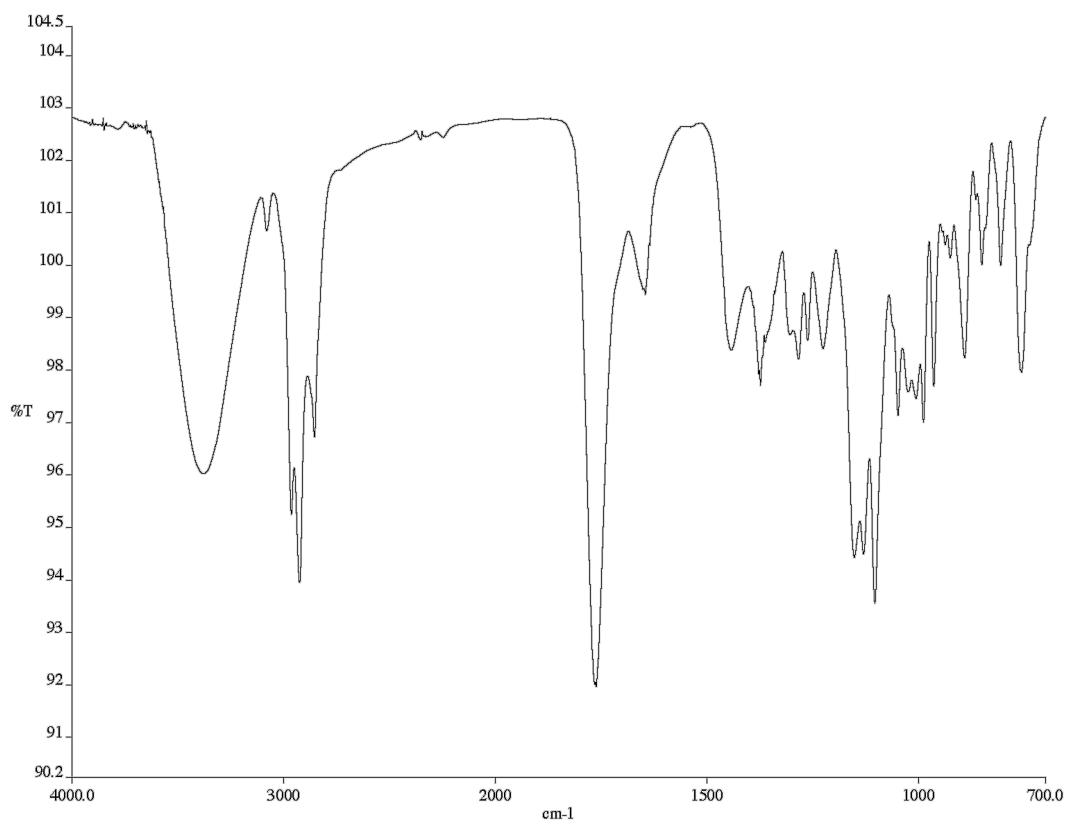
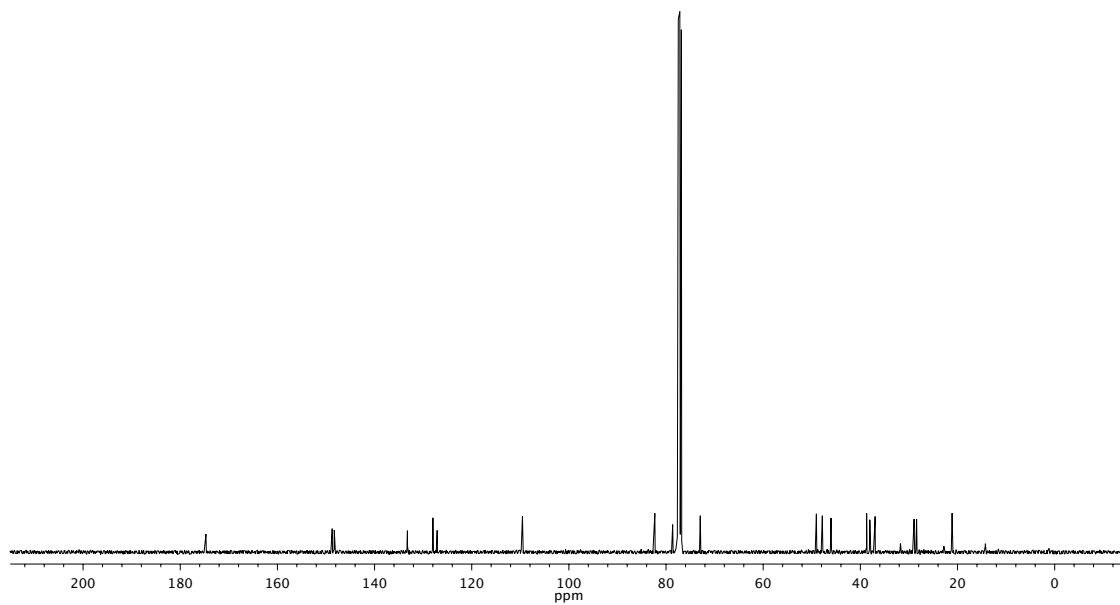


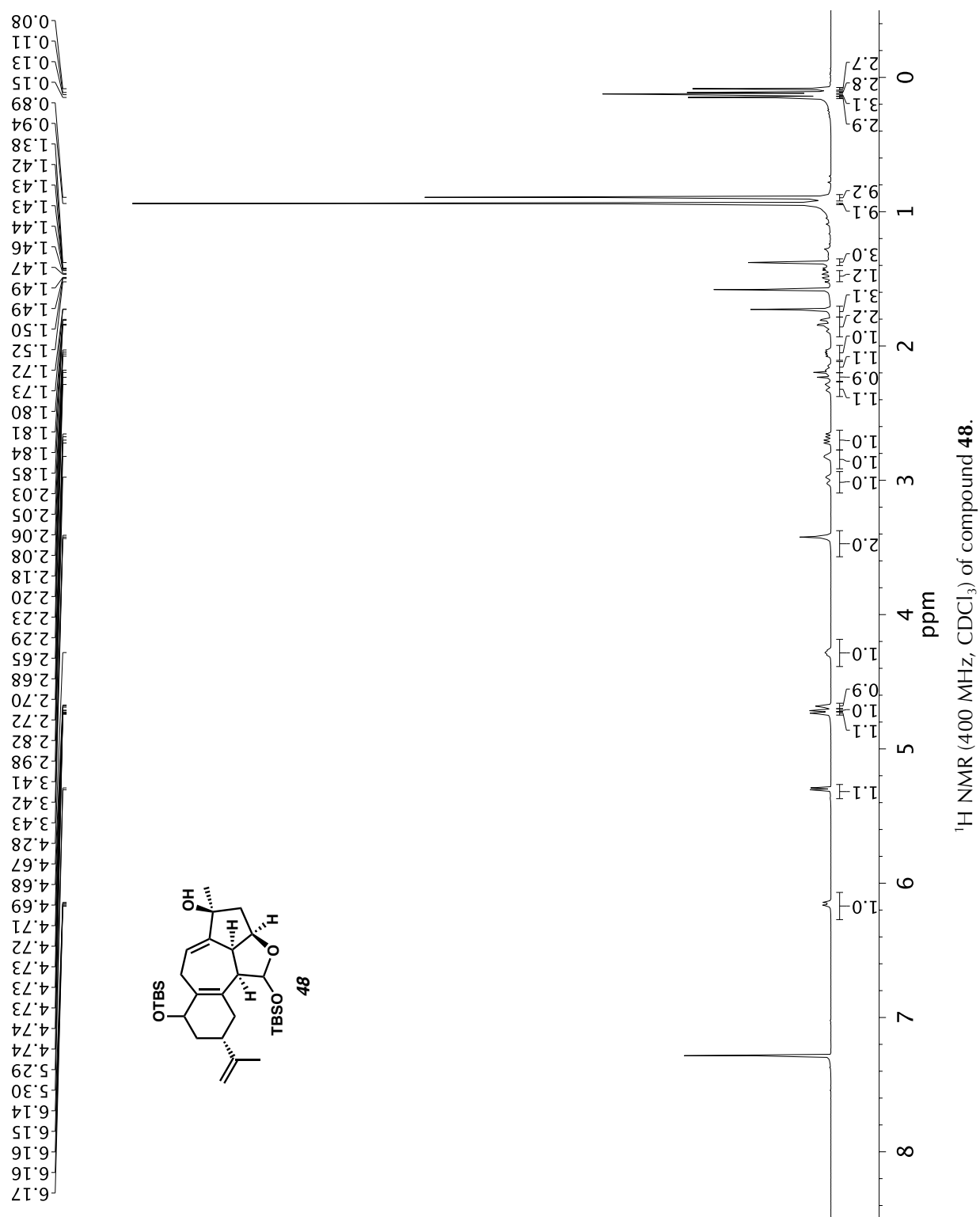
Infrared spectrum (Thin Film, NaCl) of compound **45**.¹³C NMR (101 MHz, CDCl₃) of compound **45**.

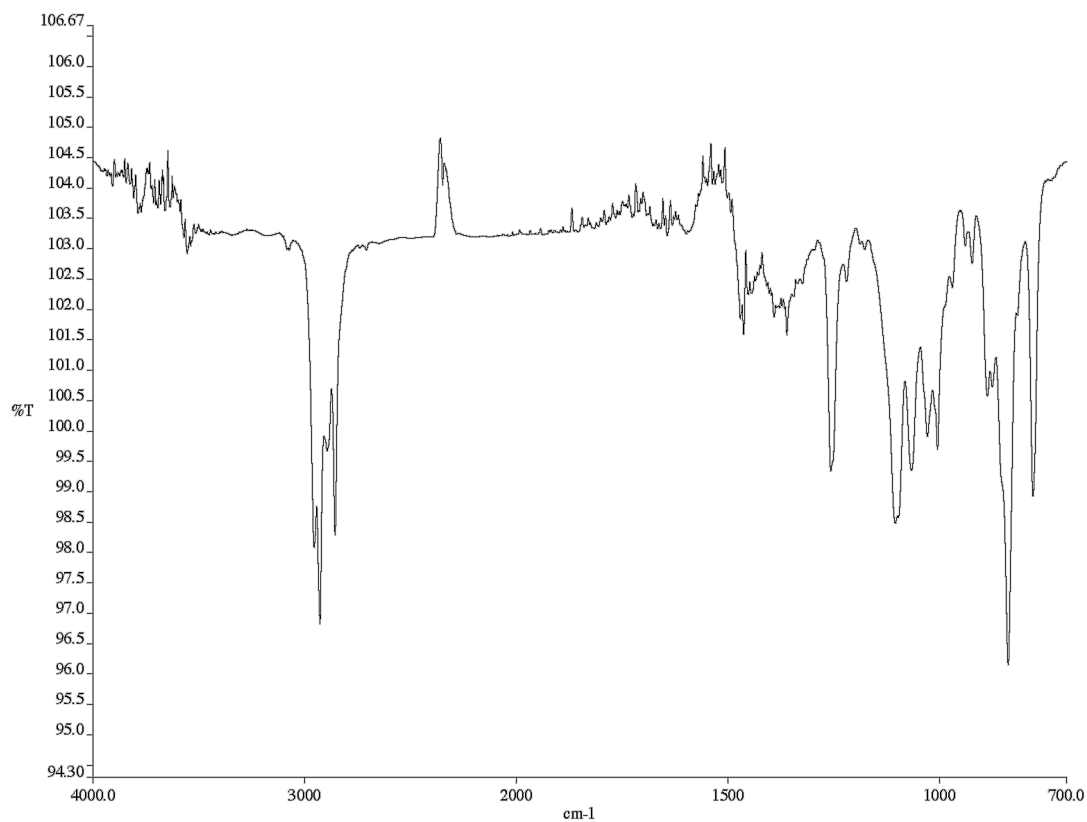
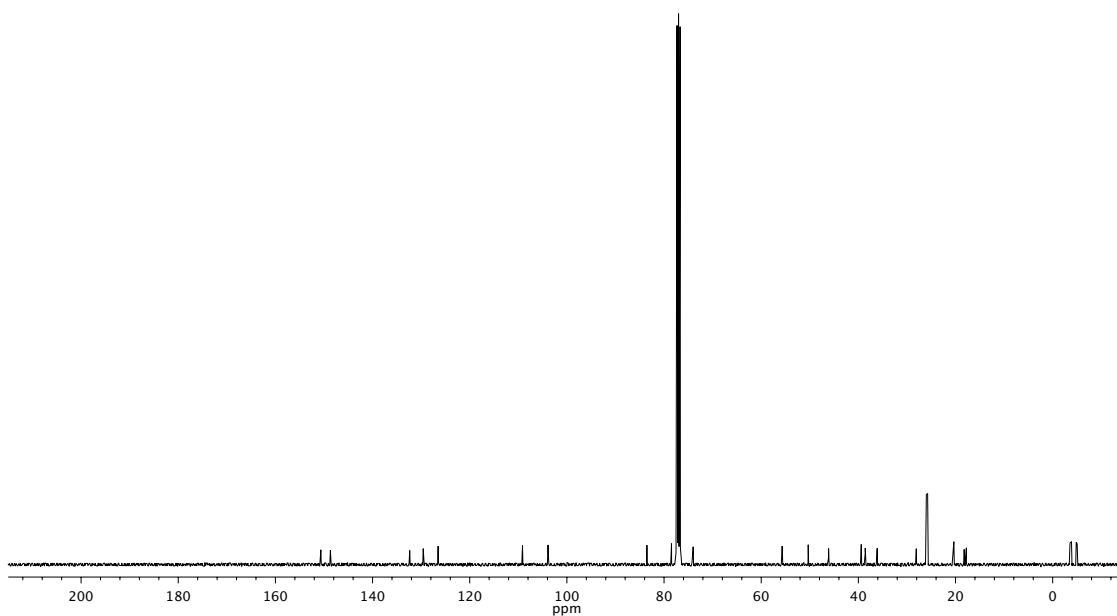


Infrared spectrum (Thin Film, NaCl) of compound **46**.¹³C NMR (101 MHz, CDCl₃) of compound **46**.

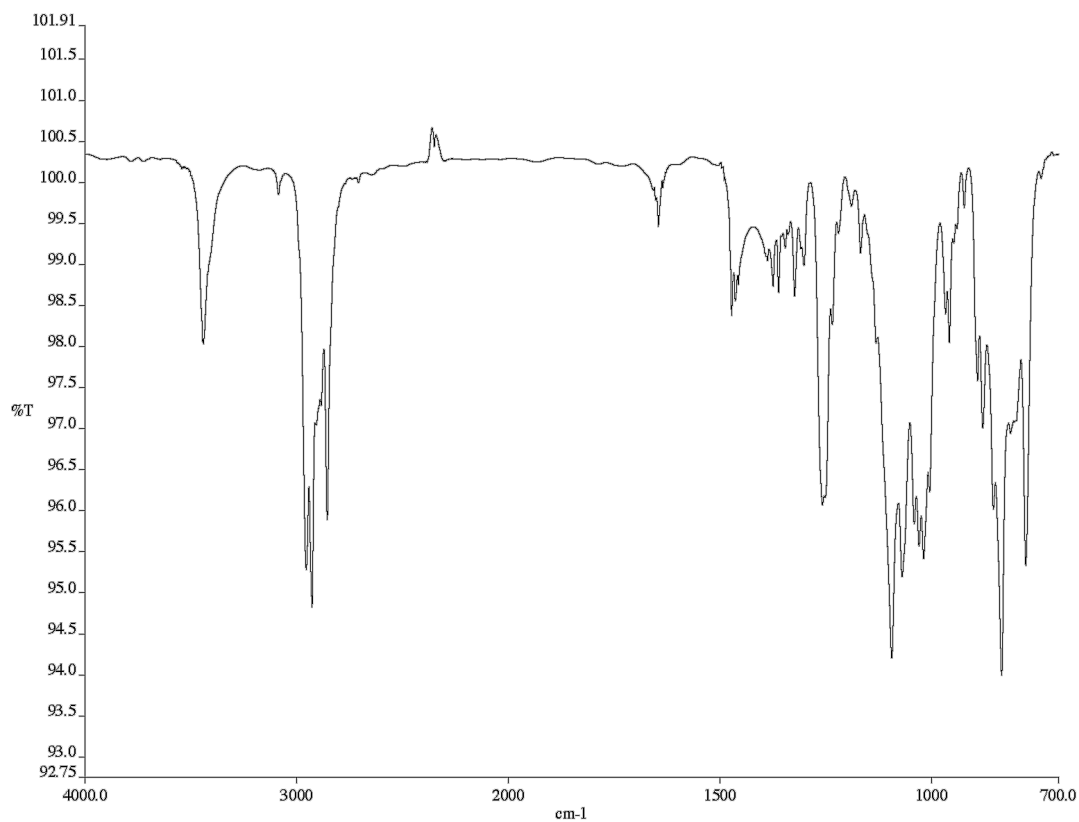
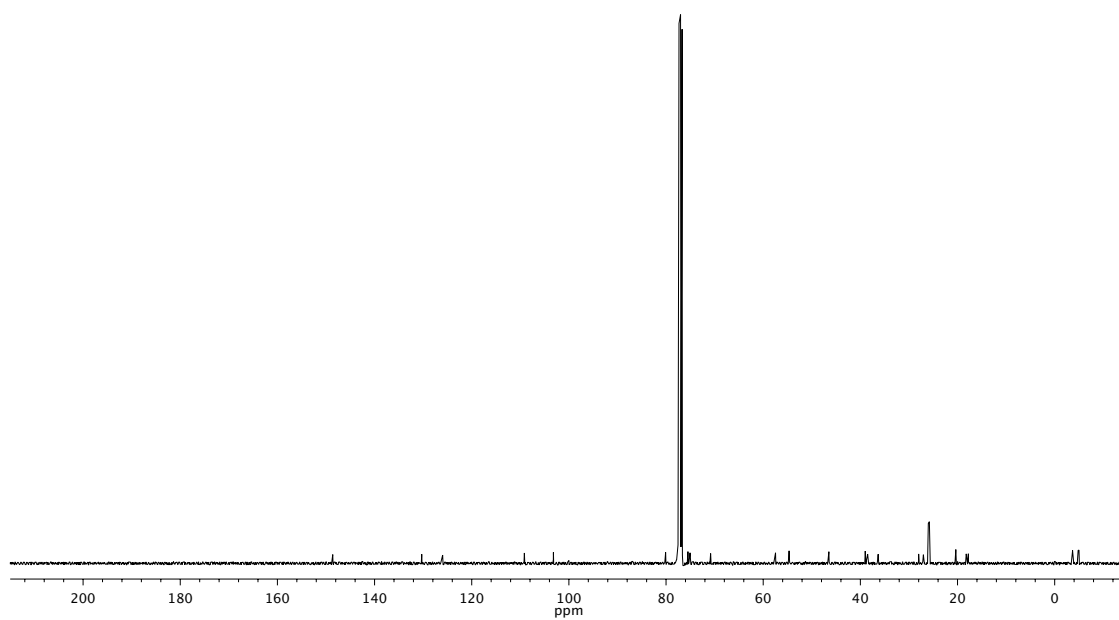


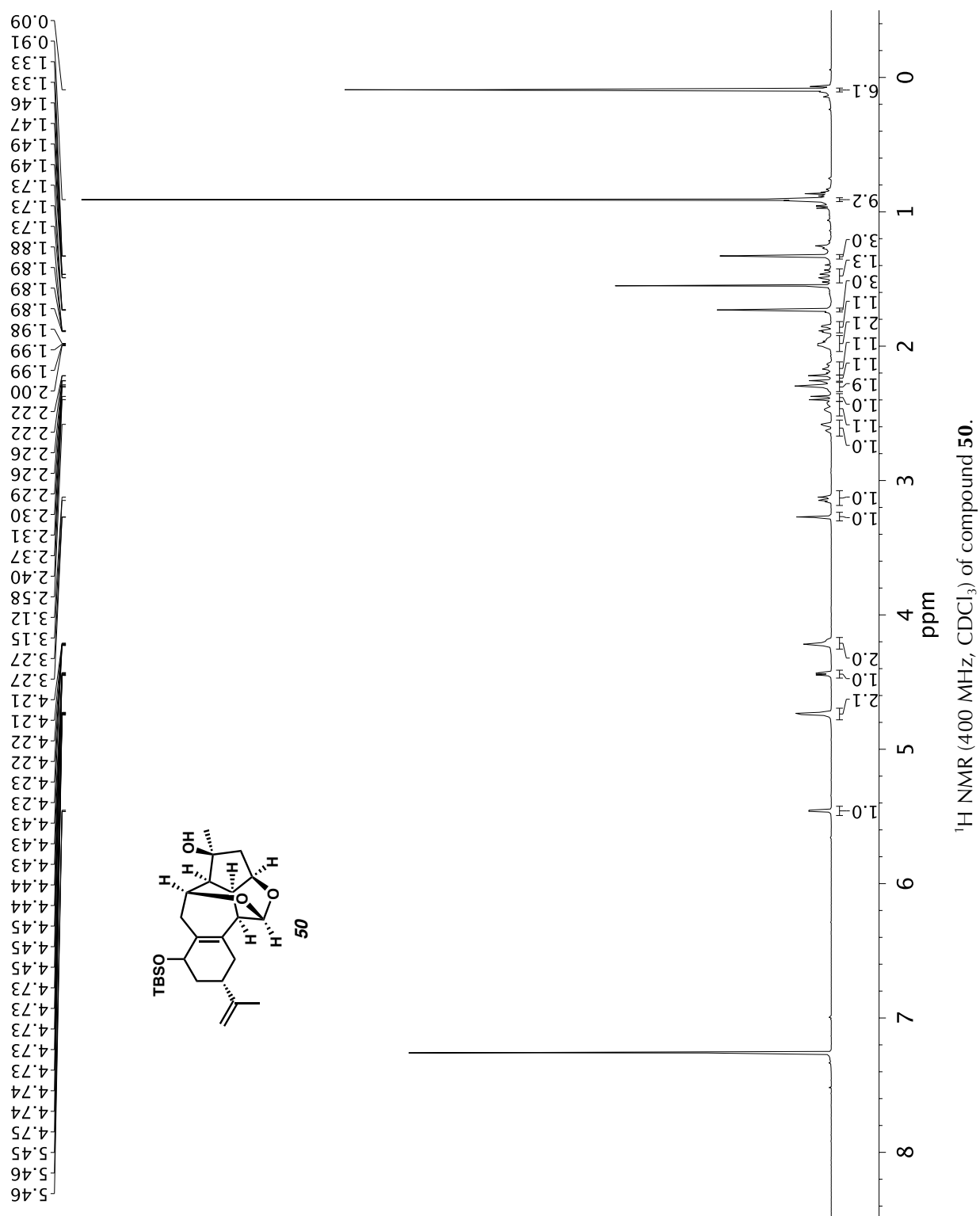
Infrared spectrum (Thin Film, NaCl) of compound **47**.¹³C NMR (101 MHz, CDCl₃) of compound **47**.

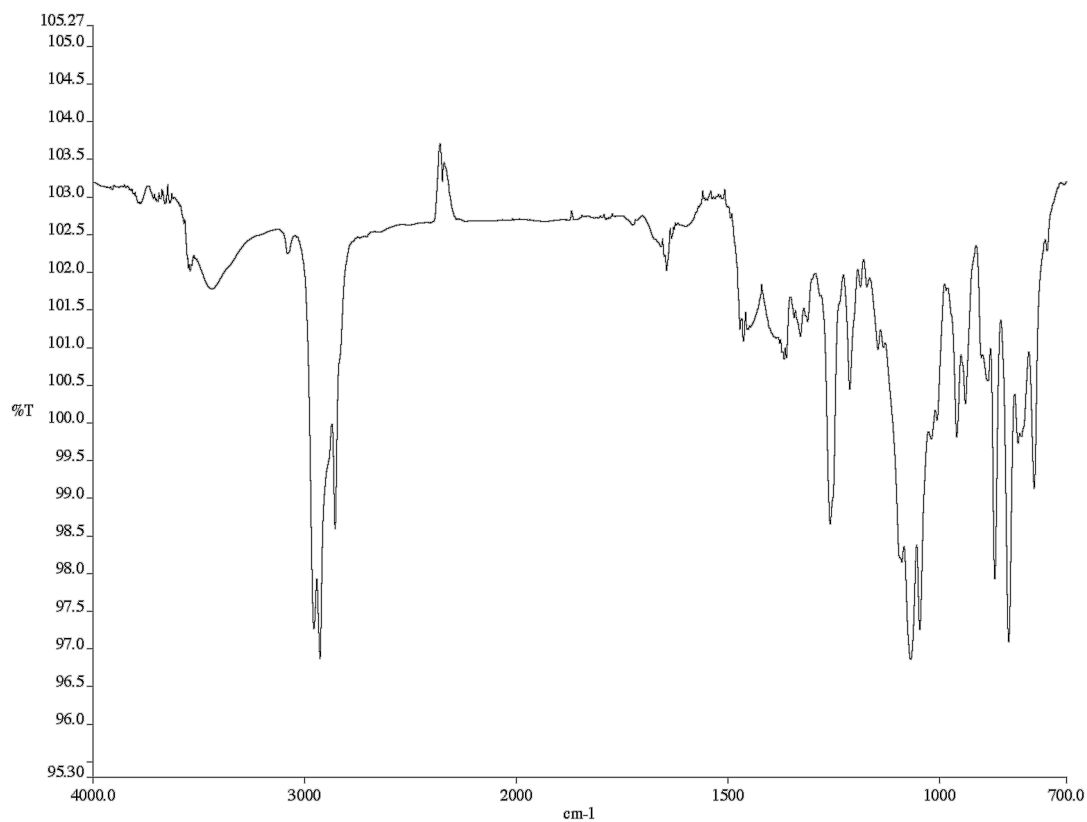
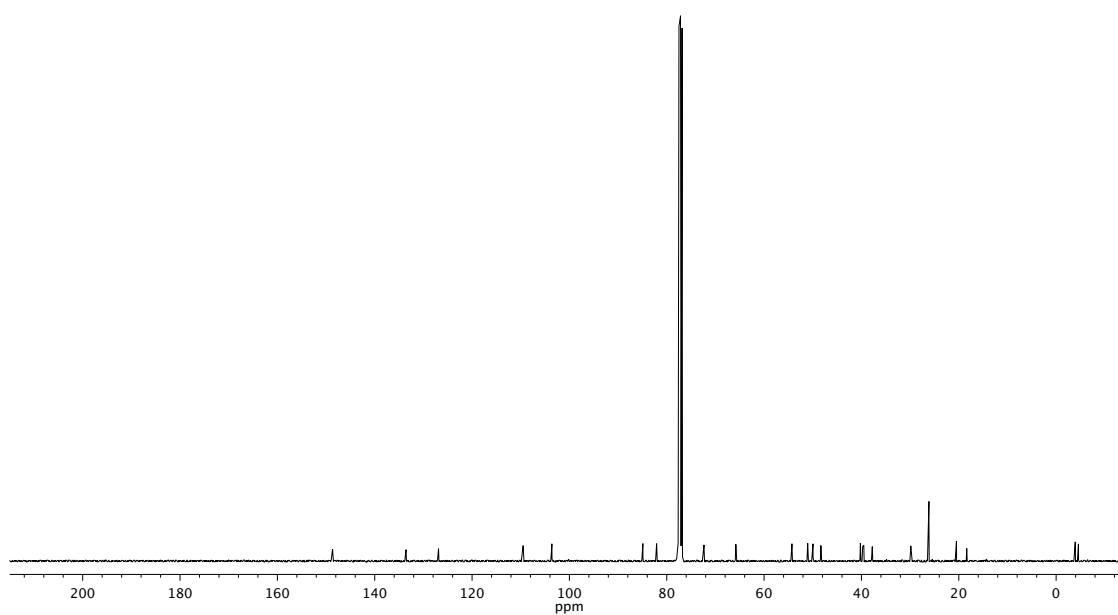


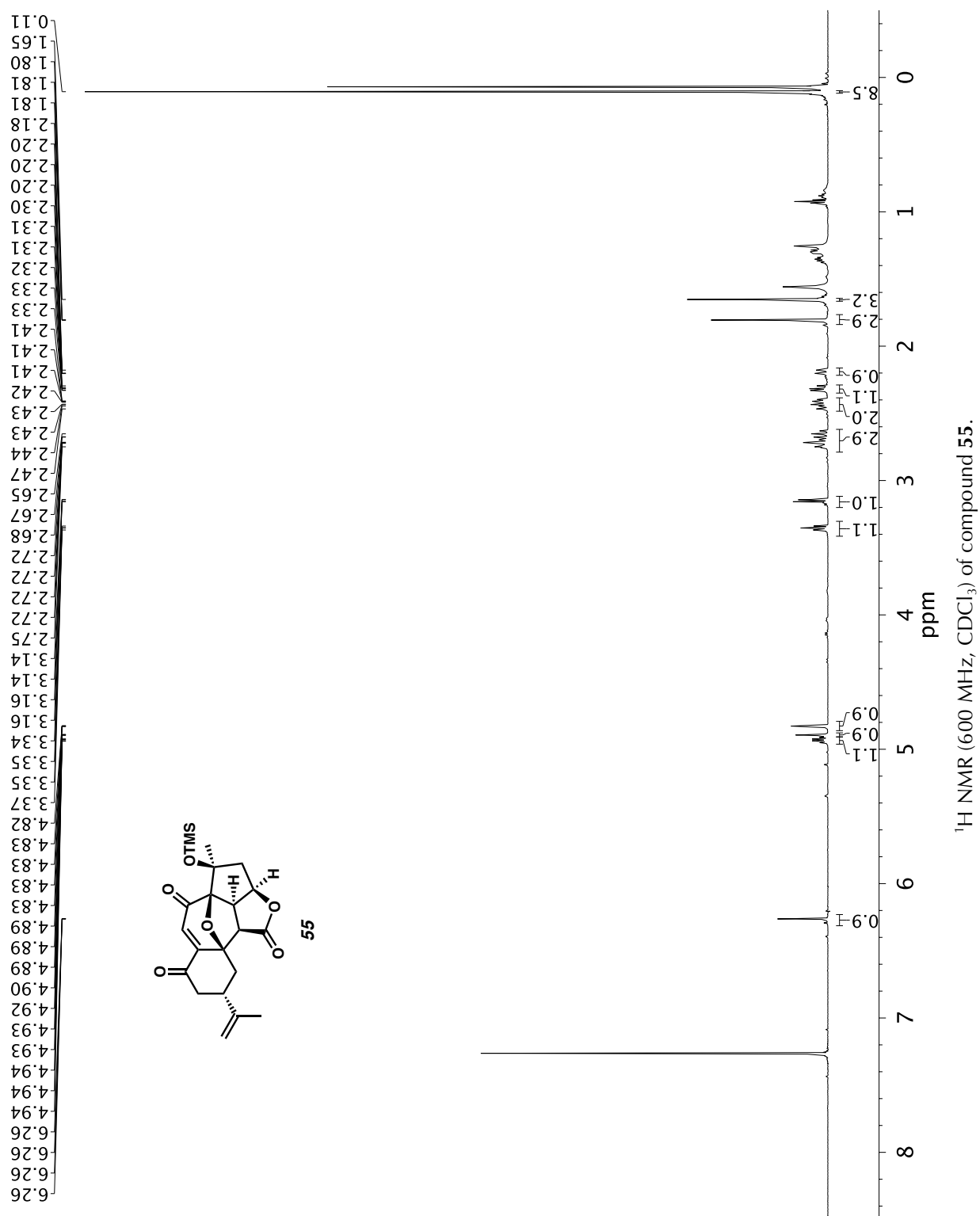
Infrared spectrum (Thin Film, NaCl) of compound **48**.¹³C NMR (101 MHz, CDCl₃) of compound **48**.

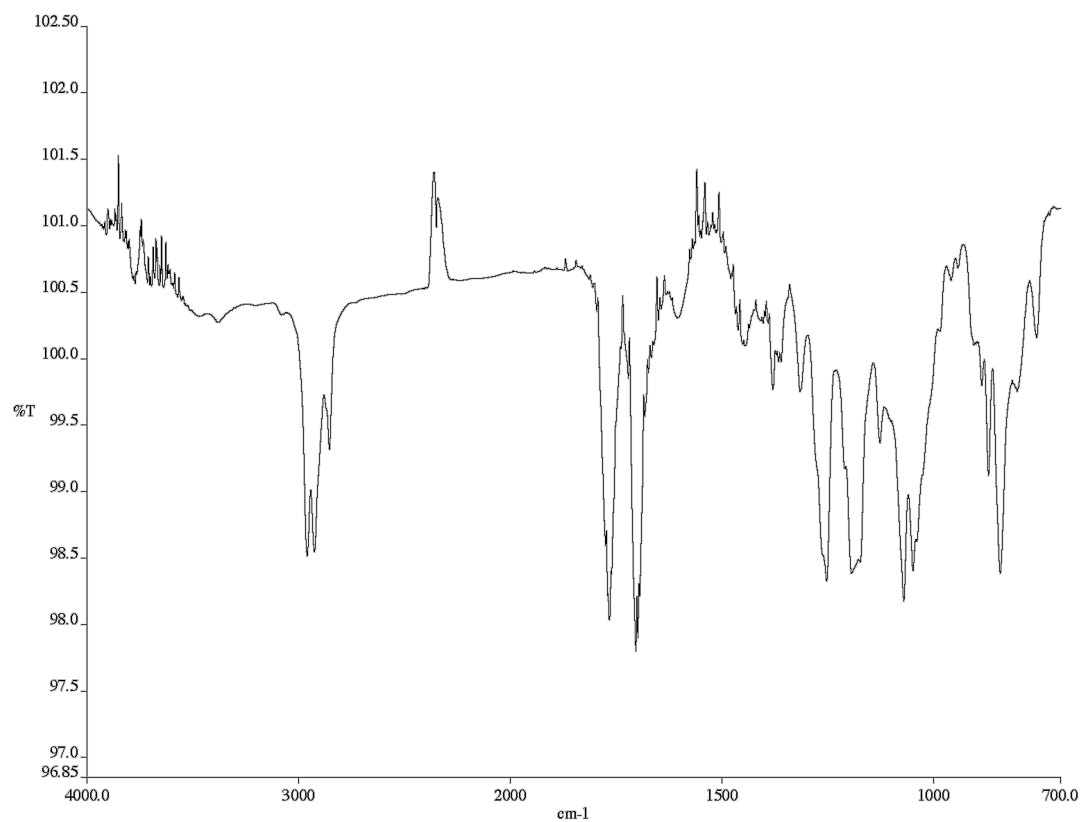
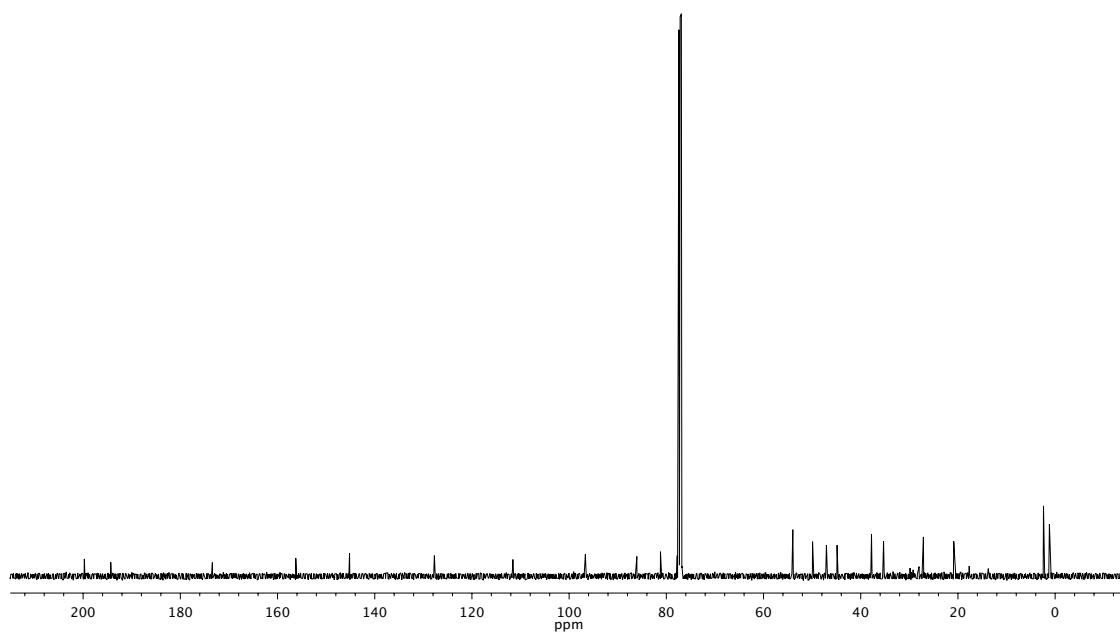


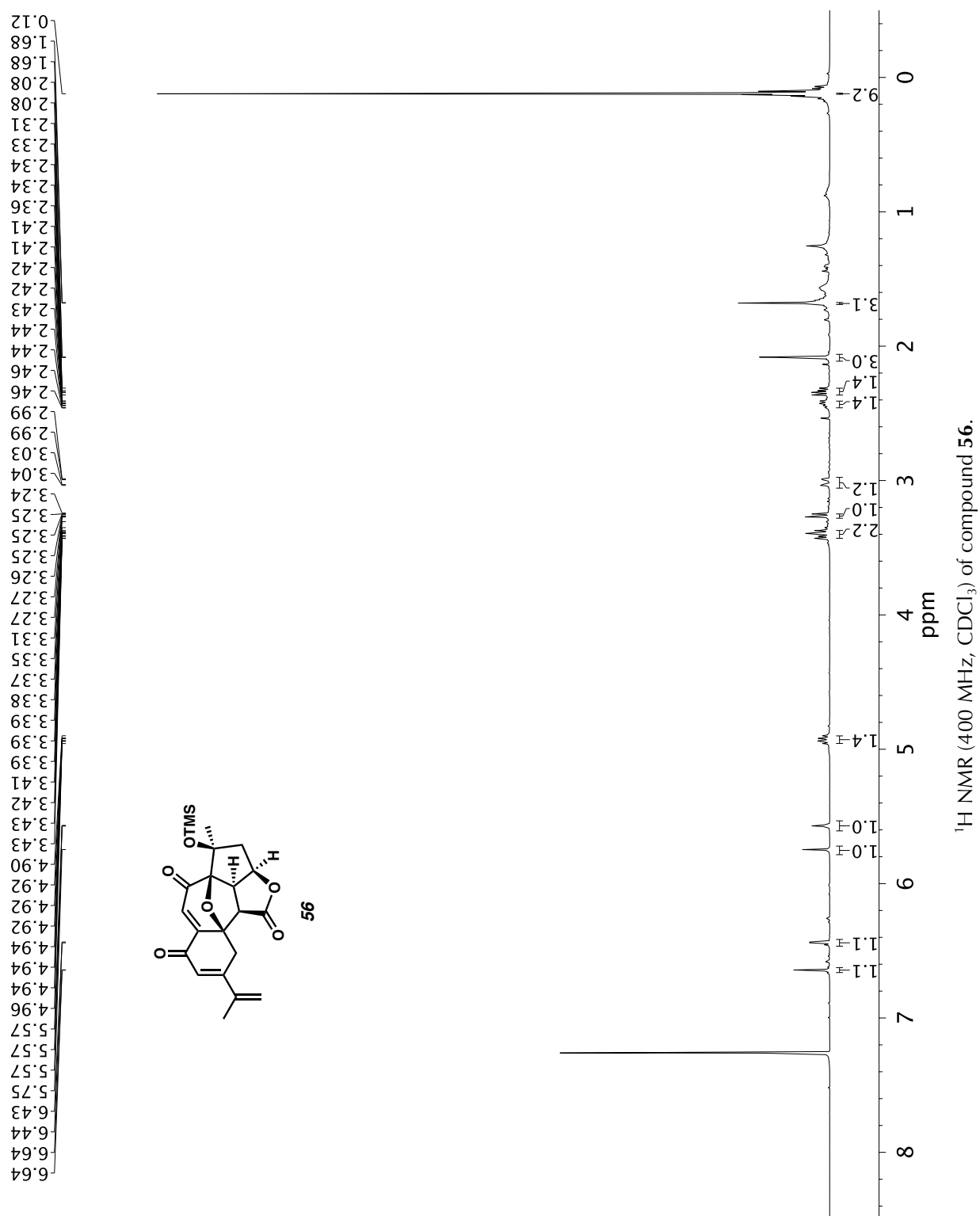
Infrared spectrum (Thin Film, NaCl) of compound **49**.¹³C NMR (101 MHz, CDCl₃) of compound **49**.

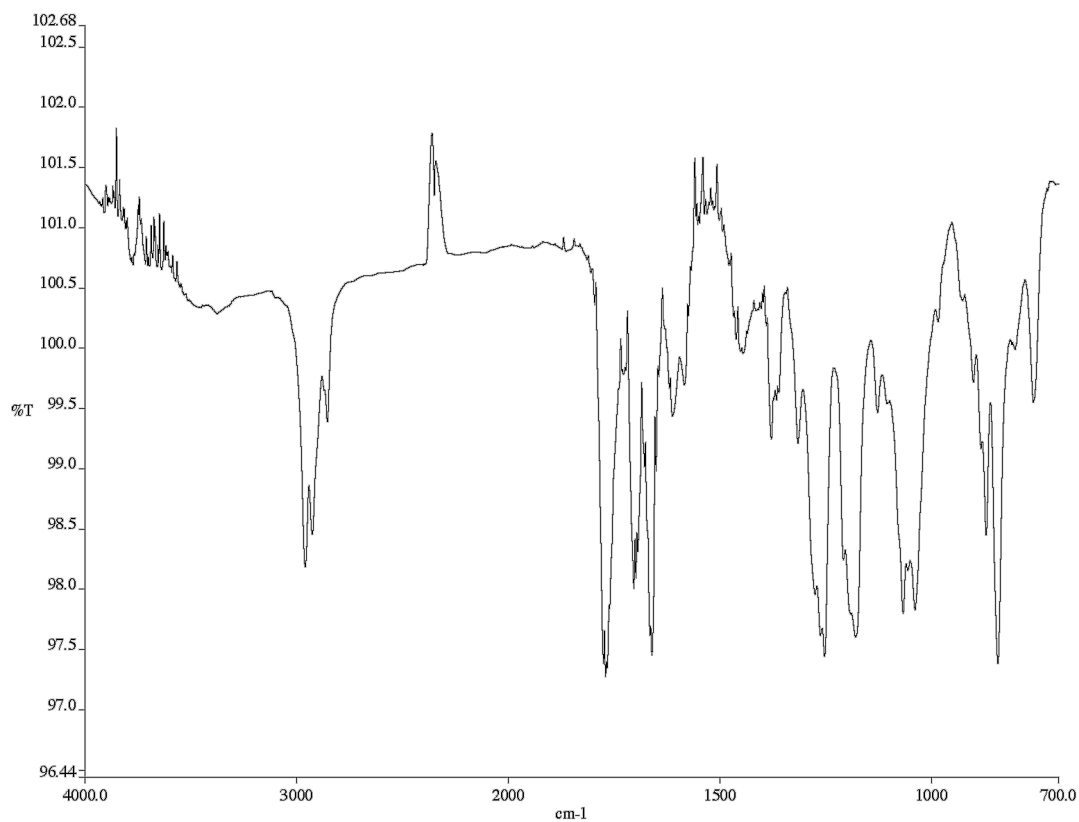
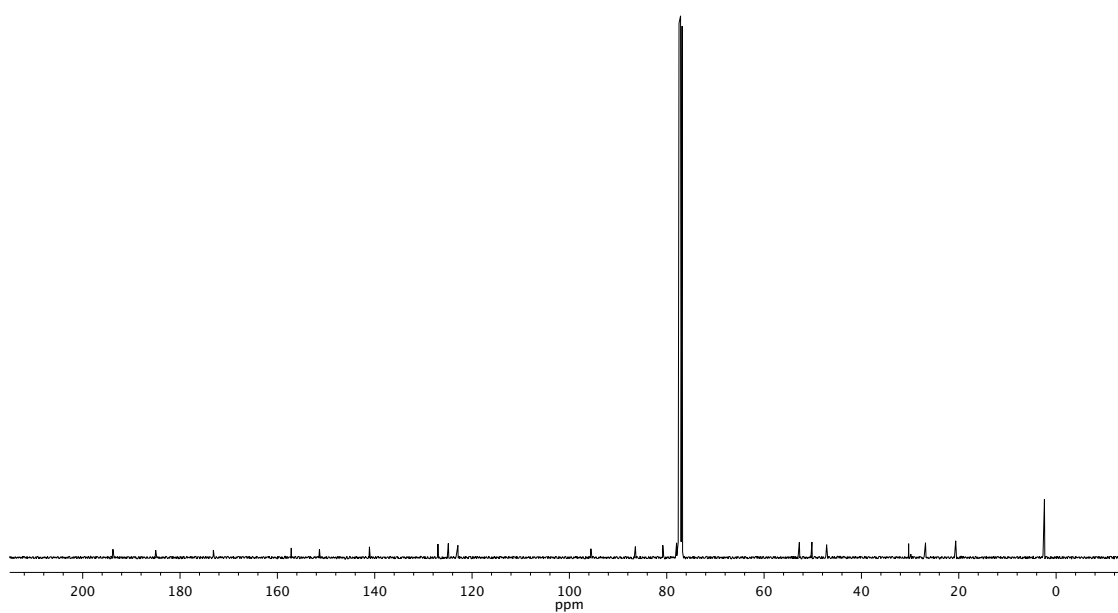


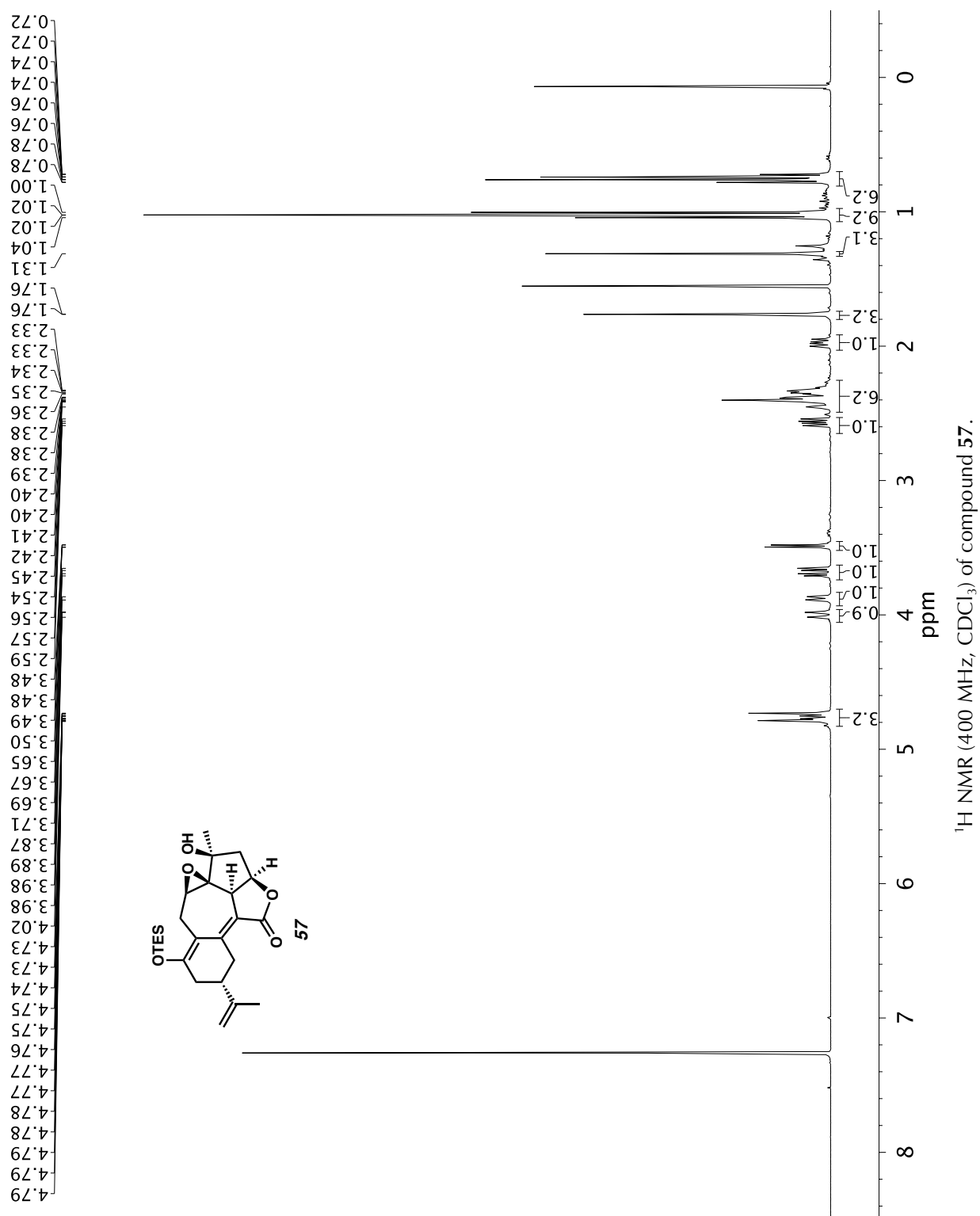
Infrared spectrum (Thin Film, NaCl) of compound **50**.¹³C NMR (101 MHz, CDCl₃) of compound **50**.

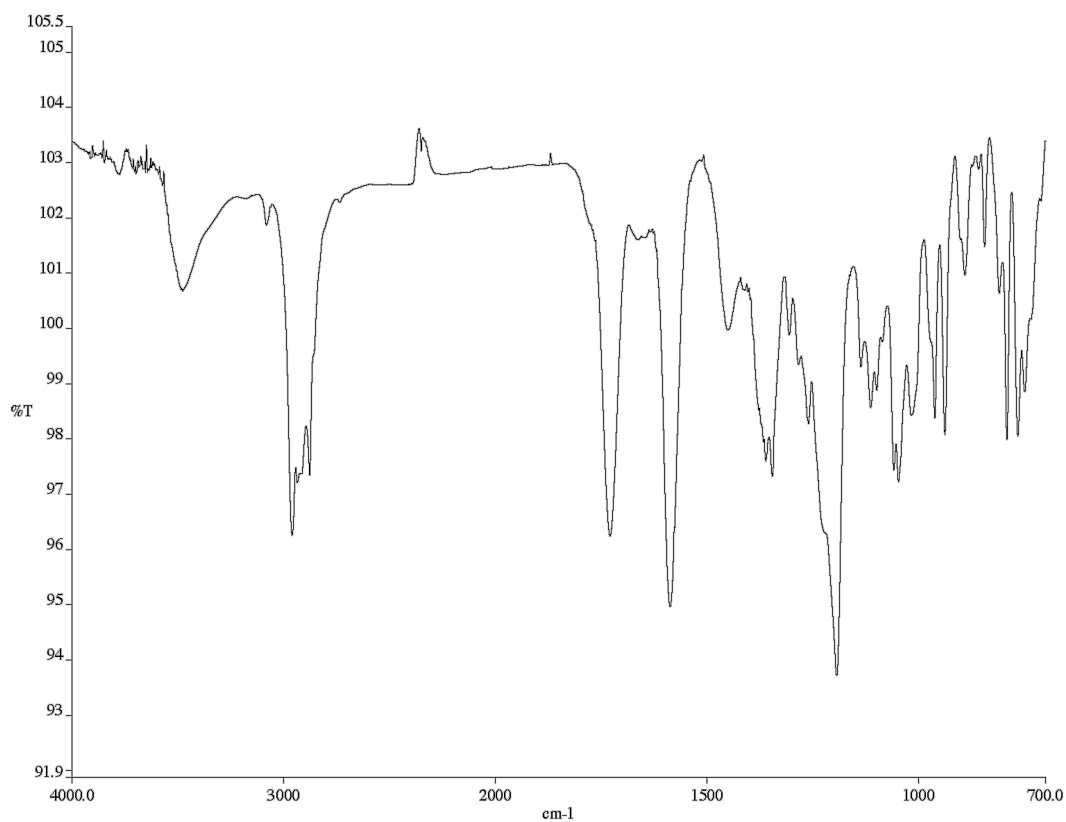
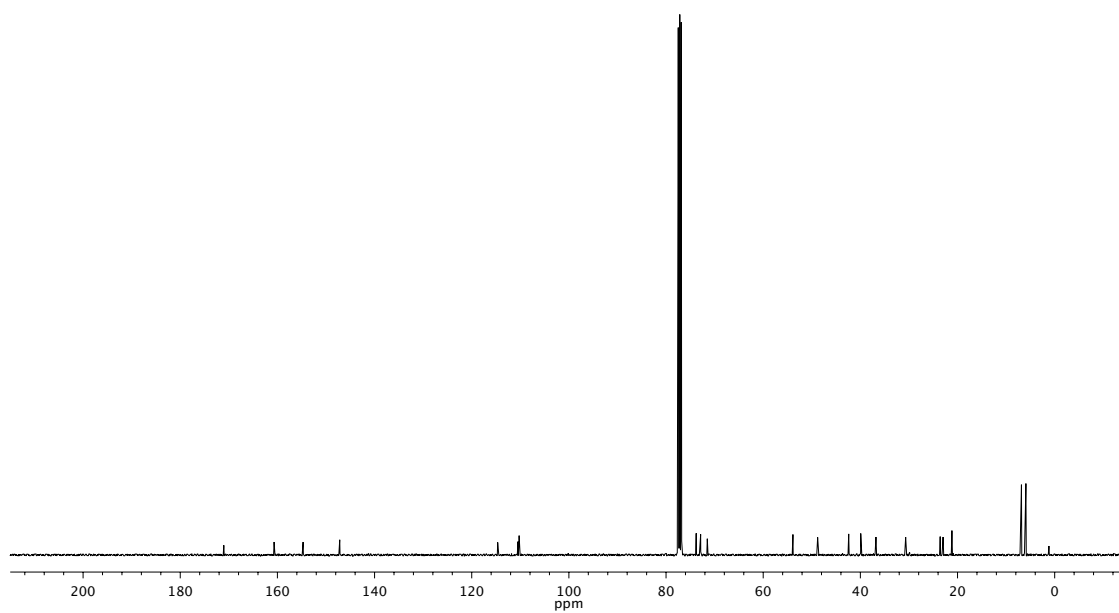


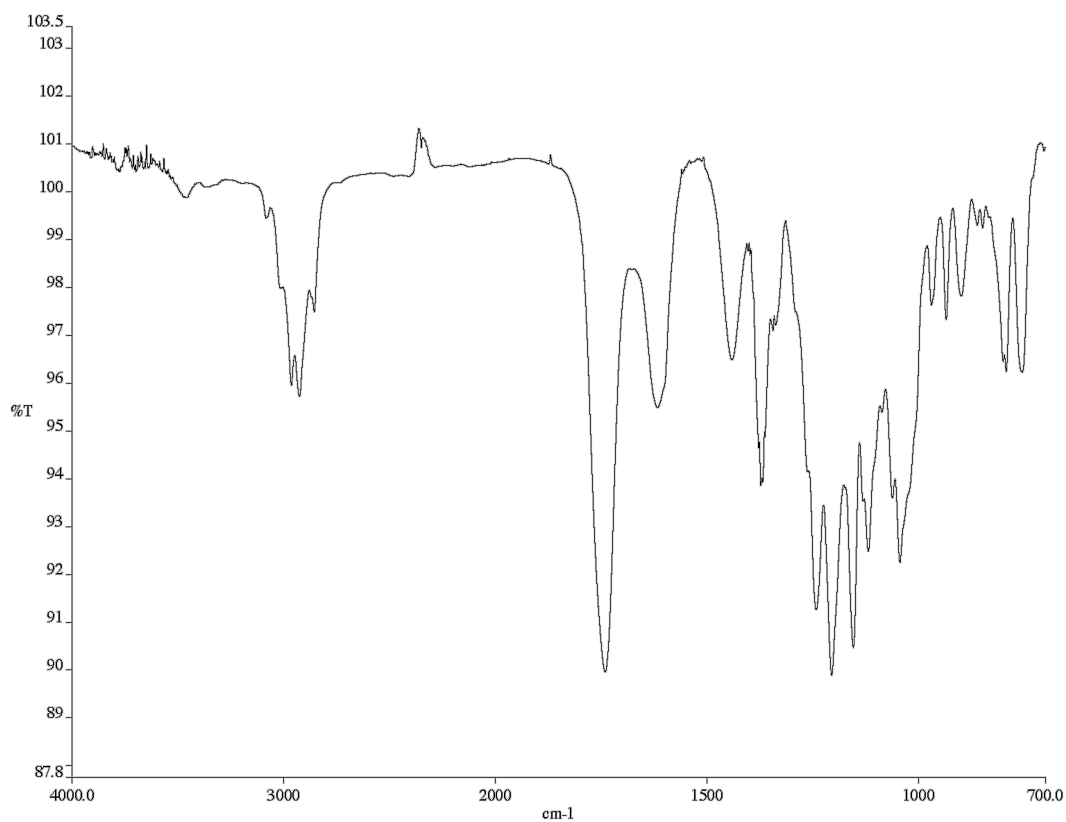
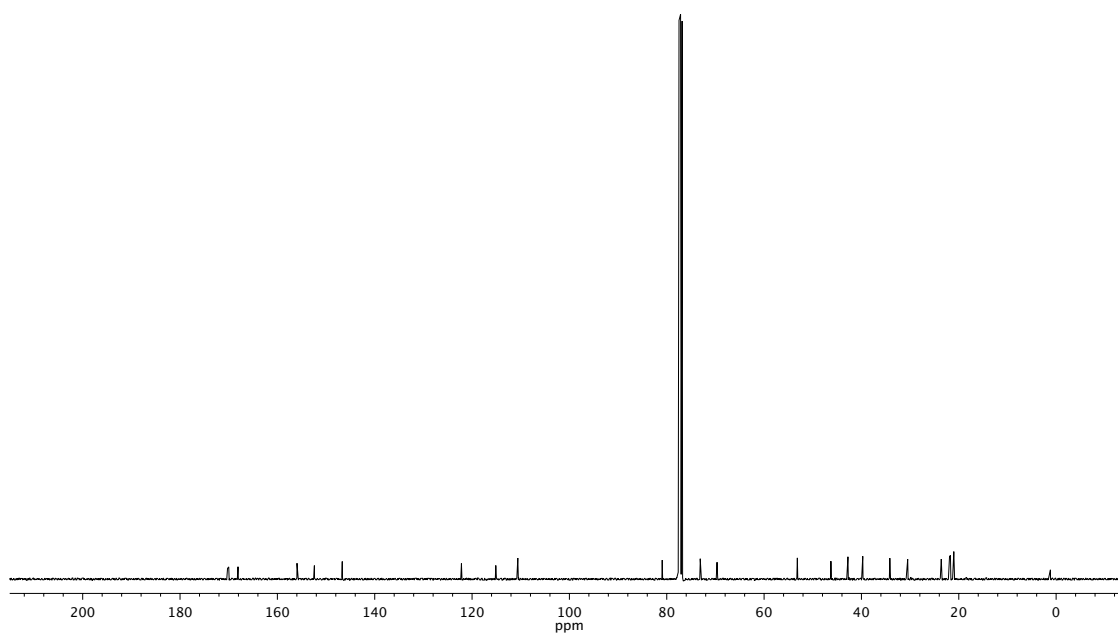
Infrared spectrum (Thin Film, NaCl) of compound **55**.¹³C NMR (126 MHz, CDCl₃) of compound **55**.

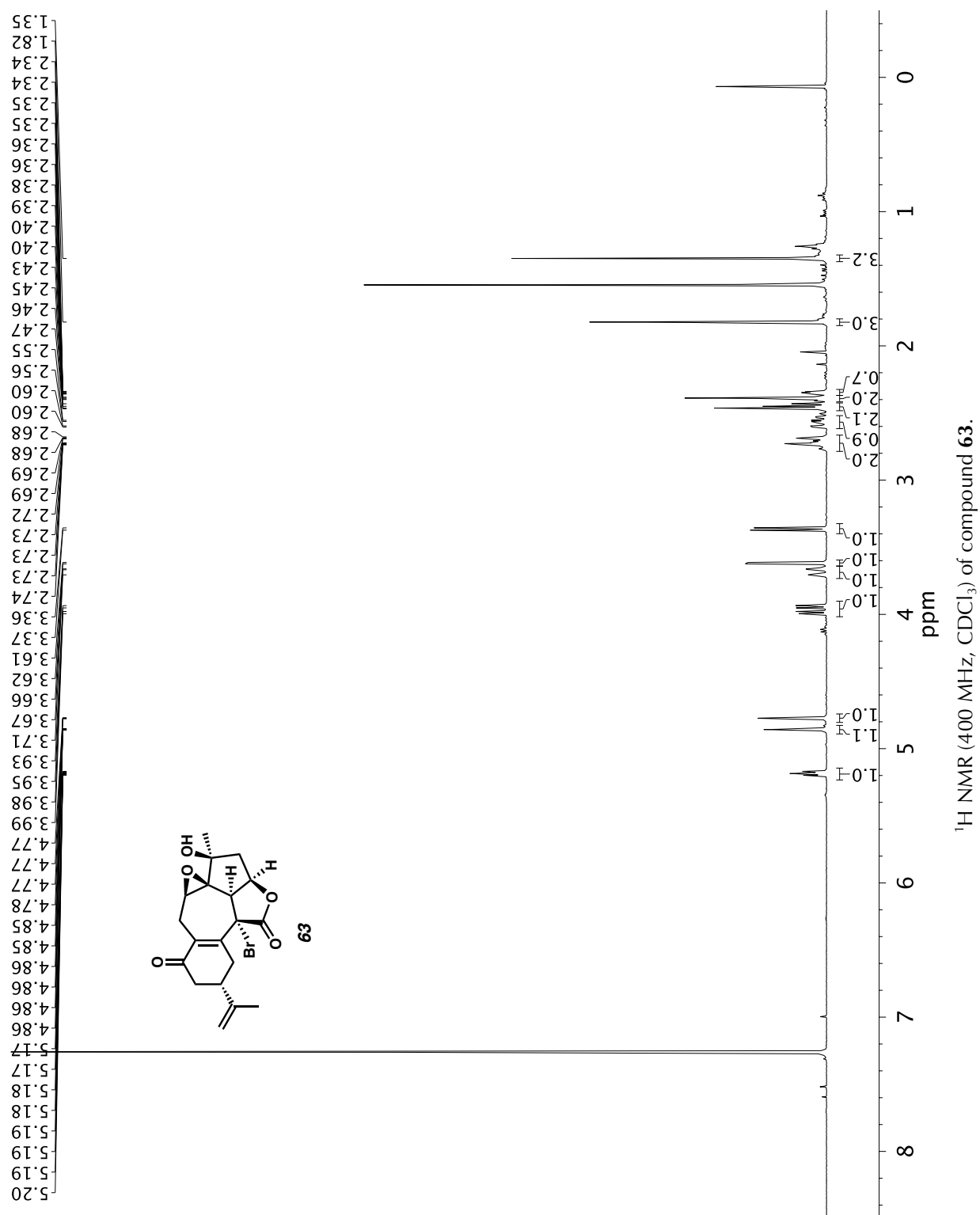


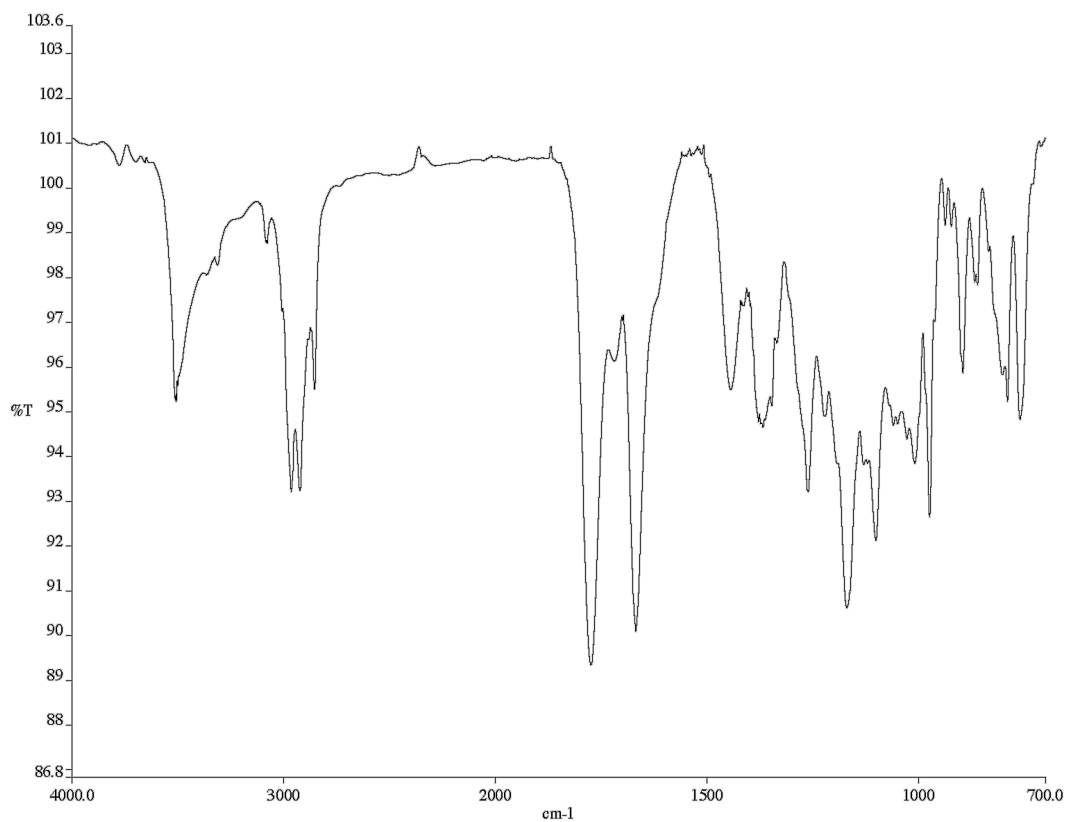
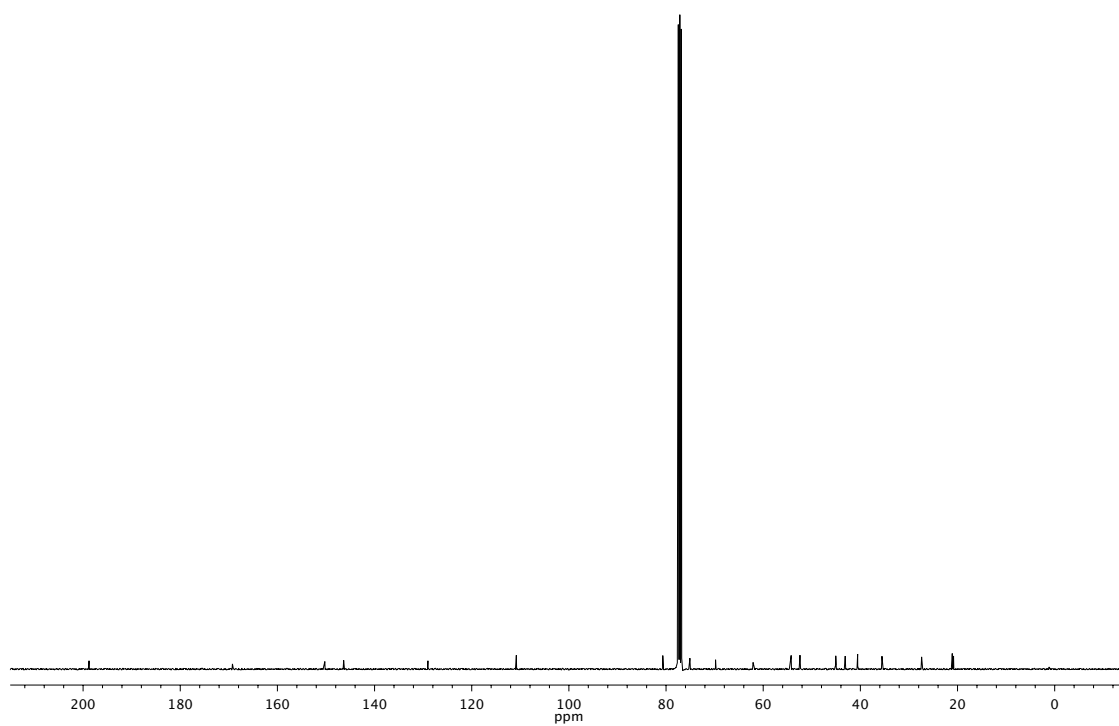
Infrared spectrum (Thin Film, NaCl) of compound **56**.¹³C NMR (101 MHz, CDCl₃) of compound **56**.



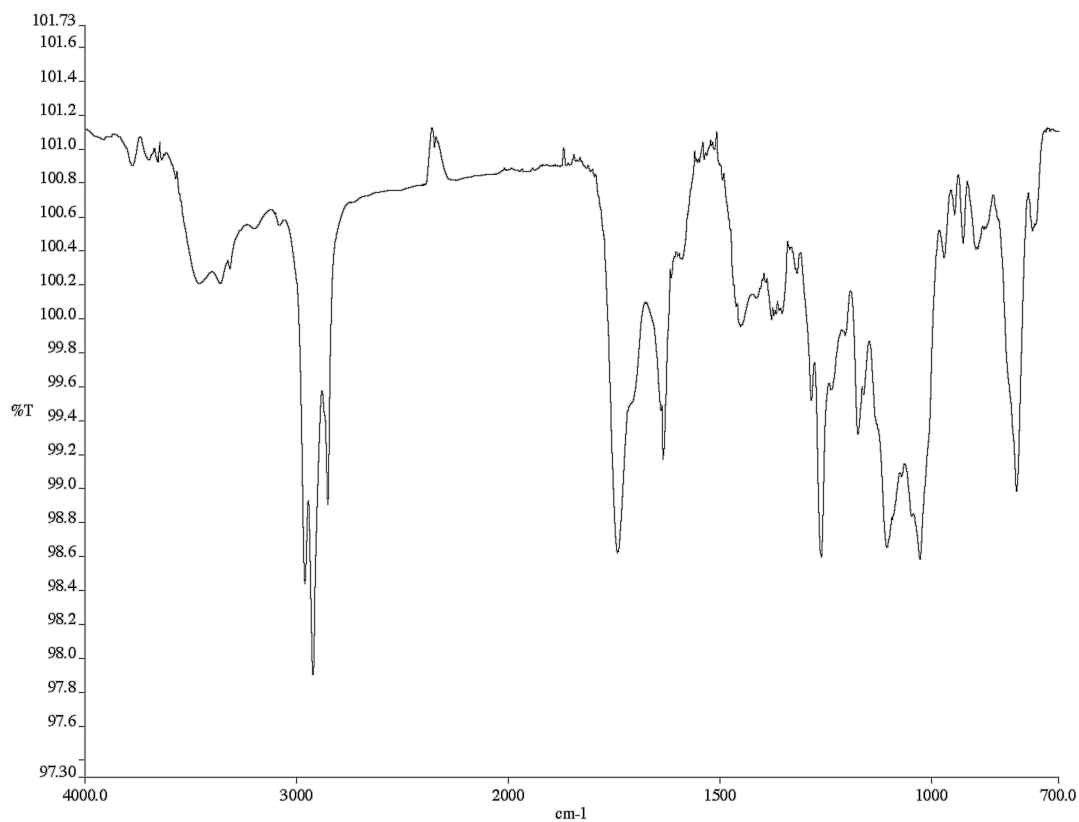
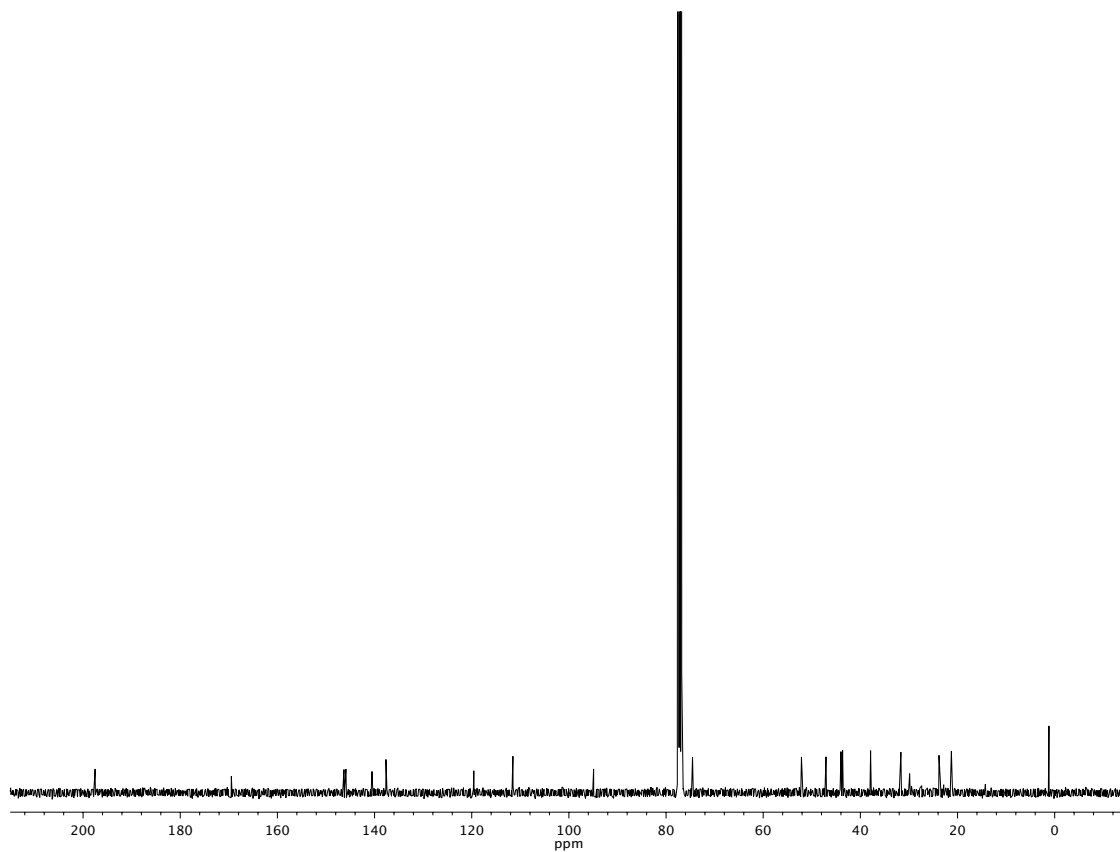
Infrared spectrum (Thin Film, NaCl) of compound **57**.¹³C NMR (101 MHz, CDCl₃) of compound **57**.

Infrared spectrum (Thin Film, NaCl) of compound **58**.¹³C NMR (101 MHz, CDCl₃) of compound **58**.

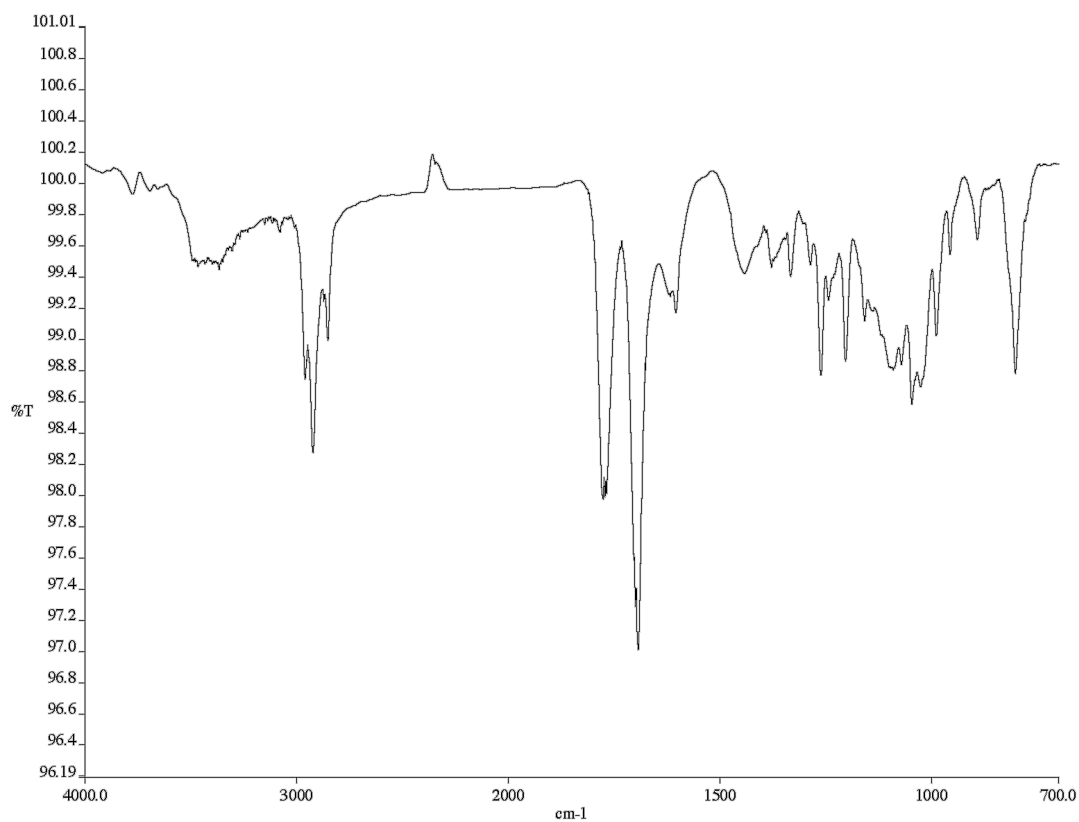
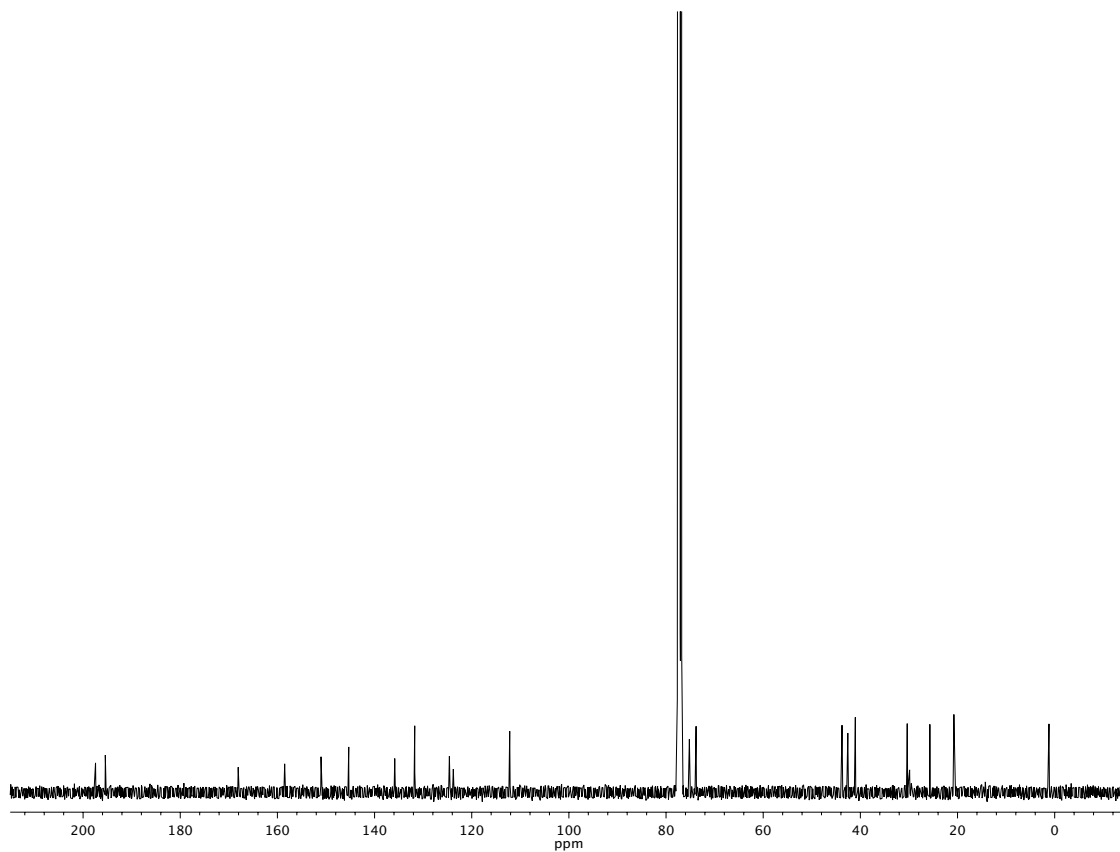


Infrared spectrum (Thin Film, NaCl) of compound **63**.¹³C NMR (101 MHz, CDCl₃) of compound **63**.



Infrared spectrum (Thin Film, NaCl) of compound **65**.¹³C NMR (101 MHz, CDCl₃) of compound **65**.



Infrared spectrum (Thin Film, NaCl) of compound **66**.¹³C NMR (101 MHz, CDCl₃) of compound **66**.